

National Oceanography Centre

Internal Document No. 01

Operating manual for the Marianda (Versatile INstrument
for the Determination of Titration Alkalinity) VINDTA 3C
for the laboratory based determination of Total Alkalinity
and Total Dissolved Inorganic Carbon in seawater

S E Hartman, C Dumousseaud & A Roberts

2011

National Oceanography Centre, Southampton
University of Southampton Waterfront Campus
European Way
Southampton
Hants SO14 3ZH
UK

Author contact details
Tel: +44 (0)23 8059 6343
Email: suh@noc.soton.ac.uk

(DEFRA contract ME 4133 - “DEFRApH”)

DEFRApH - Sample collection and handing procedures: DEFRApH - A study to define the present state of UK waters with respect to potential changes in the degree of acidification (pH) of these waters; combining collection of new data over two years, review of pre-existing information and numerical analysis. **Operating manual for the Marianda (Versatile INstrument for the Determination of Titration Alkalinity) VINDTA 3C for the laboratory based determination of Total Alkalinity and Total Dissolved Inorganic Carbon in seawater.**

DOCUMENT DATA SHEET

<i>AUTHOR</i> HARTMAN, S E, DUMOUSSEAUD, C & ROBERTS, A	<i>PUBLICATION DATE</i> 2011
<i>TITLE</i> Operating manual for the Marianda (Versatile Instrument for the Determination of Titration Alkalinity) VINDTA 3C for the laboratory based determination of Total Alkalinity and Total Dissolved Inorganic Carbon in seawater.	
<i>REFERENCE</i> Southampton, UK: National Oceanography Centre, Southampton, 66pp. (National Oceanography Centre Internal Document, No. 01) (Unpublished manuscript)	
<i>ABSTRACT</i> <p>All chemical and biogeochemical process in the sea are affected by the acidity of the water. Acidity is therefore fundamental property of seawater. The growing concern that the acidity of the oceans might be increasing has revealed weaknesses in our knowledge of this fundamental property and its variation in space and time.</p> <p>In 2008 the DEFRApH project (DEFRA contract ME4133) was initiated to provide this missing information in UK related waters. It required sampling for and analysis of the total inorganic carbon (DIC) and total alkalinity (TA) content of samples. This report documents the procedures used for operation of the VINDTA 3C analysis instrument (manufactured by Ludger Mintrop, Marianda, Kiel, Germany) developed at NOC since 2005. It covers instrument set up, daily procedures and the calculation of the final reported concentrations.</p>	
<i>KEYWORDS</i> Analysis, Calculation, Operation, Total alkalinity, Total inorganic carbon, Trouble Shooting	
<i>ISSUING ORGANISATION</i> National Oceanography Centre, Southampton University of Southampton, Waterfront Campus European Way Southampton SO14 3ZH UK	
<i>Not generally distributed - please refer to author</i>	

Contents

Section	page
Overview	
1. Start-Up	9
1.1. Preparing The Equipment:	10
1.2. Software Start-Up	13
1.3. Running Junks	16
1.4. Running Sub-Standards	17
1.5. Checking The Blank	18
1.6. Assessing Accuracy Using Certified Reference Material (CRM) seawater samples	19
2. Running DIC And TA Samples	21
3. Calculating Results	23
3.1. Running Matlab To Process Samples	24
3.2. CO2 Sys Program To Calculate Other Carbonate Variables	26
4. Vindta Shut Down Procedure	28
4.1. Daily Shutdown	28
4.2. Extended Shutdown ('Hibernation')	29
5. Maintenance	30
6. Appendix	31
6.1. Preparation Of Chemicals	31
6.2. Calibrating The Pipettes	32
6.3. Temperature Sensor Calibration	34
6.4. Preparing The Scrubbing Cells	34
6.5. Troubleshooting and "Top Tips"	35
6.6. Vindta Parts List	47
6.7. Additional Vindta Photo Guides:	49
6.8. Example Of The CRM Certificate Of Analysis And Precision	52
6.9. Risk Assessment For The VINDTA 3C	53
6.10. Sample Processing	57
6.11. Contact Details:	65

Overview

The VINDTA (Versatile INstrument for the Determination of Total Alkalinity) system will measure Total Alkalinity of seawater. The 3C versions at NOC also measures DIC on the same sample. The VINDTA system consists of two pipettes: the larger (volume of approximately 100 ml) receives the sample to measure total alkalinity (AT) and feeds it into the Titrino cell where it is titrated with HCl (added in 0.15 ml increments). This alkalinity titration is followed using an electrode and the two endpoints are determined using software. The smaller (volume of approximately 20 ml) pipette receives the sample that feeds into the stripper where phosphoric acid converts the DIC (total carbonate) to CO₂ (water is removed using a peltier controlled condenser). The CO₂ is carried (using N₂ carrier gas) into the coulometer cell where it reacts with monoethanolamine to form a titratable acid that causes a blue indicator dye to fade. A current flows to generate base that removes the acid, causing a return to the original colour (at which point the current stops). When the indicator colour is restored, the current required is equivalent to the amount of CO₂.

The main VINDTA program will add phosphoric acid, wait for a 'clear and ready check', rinse and fill the DIC pipette then dispense it to the stripper to begin the titration. Meanwhile the alkalinity cell is rinsed with NaCl and the large pipette rinsed and filled with sample. This sample is dispensed into the cell and the alkalinity titration can then start whilst the DIC titration is underway. In this way the instrument should reduce sample handling time (compared with when the individual methods are run manually) and should also result in more precise analysis. Risk assessments are found at the end of this document and should be read with care and signed before following the procedures explained here.

When seawater samples arrive in the lab they are assigned a unique incremental 'nutrient' number straight away. Sample name uses this 3 digit nutrient number, taking the form of 'year month-nutrient number' (eg: 0905-127 for nutrient 127 from a sample in May 2009) for processing reasons described in this document. The laboratory book is used to trace this sample to its source so the unique name goes into the laboratory notebook along with all sample details from the sample label.

The HgCl₂ treated samples of sea water are placed in the 25°C water bath prior to analysis. Following analysis nutrient samples are taken to be used in Matlab processing and to assess whether silicate has leached from the sample bottle with storage. However a silicate

change of 100 μM will vary the TA reading by 0.02 $\mu\text{mol/kg}$. Salinity is also corrected for at the Matlab processing stage as a change of 5 salinity units may change the TA result by around 7 $\mu\text{mol/kg}$.

Data output is transferred from the logbook into an Excel spreadsheet kept locally on the laboratory PC. The initial AT and DIC results recorded are corrected using the Certified Reference Material (CRM) correction factor (based on the difference between the measured and certified value). The Excel sheet also contains the sub-standards run for each day to assess precision. Further density corrections are then made to DIC.

This manual has been written to accompany the VINDTA manual written by Ludger Mintrop of Marianda, the builder of the VINDTA instrument. This manual deals with day to day use of the instrument and includes guidance on common troubleshooting issues encountered during the instruments set-up and use. Any questions or issues not covered in this or the official VINDTA manual should be directed to L. Mintrop at Marianda whose contact details are on page 69.

1. *Start-up*

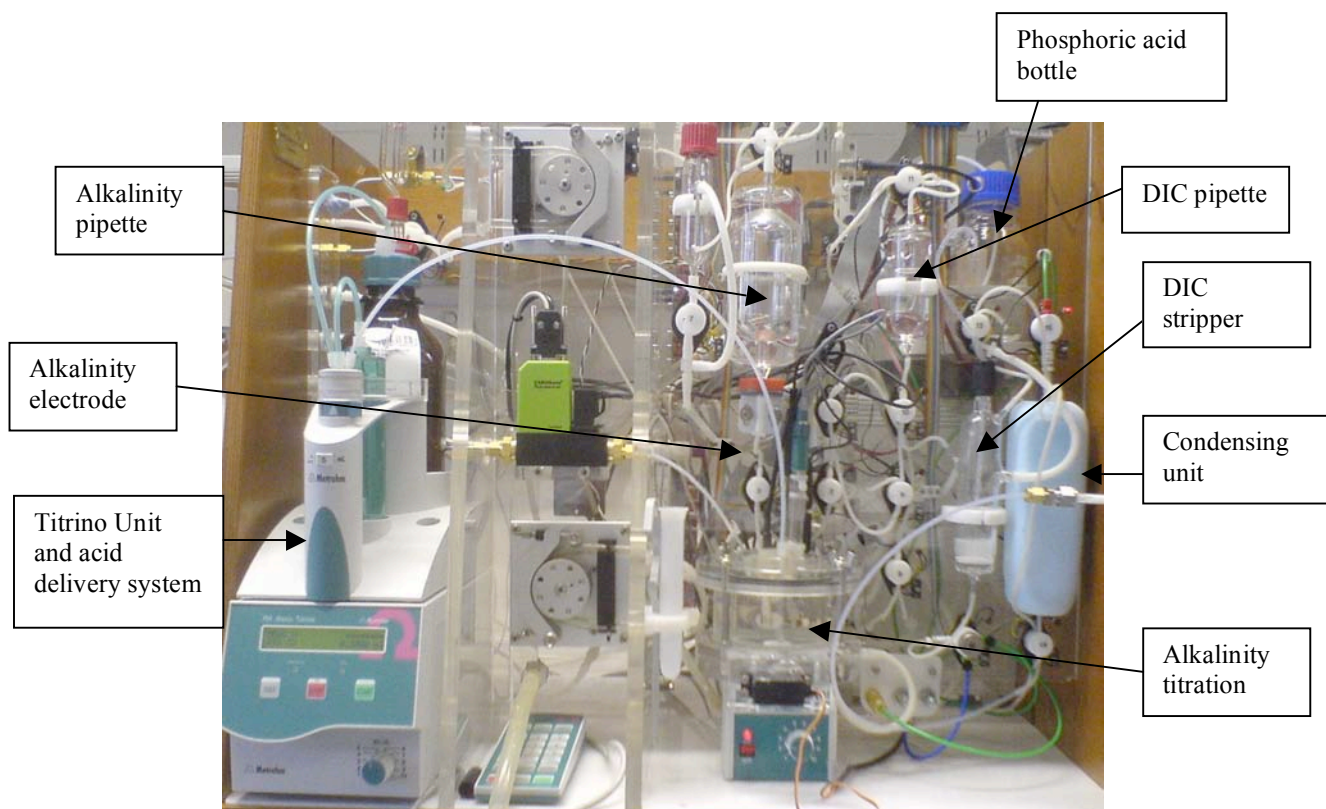


Figure 1.1 The VINDTA instrument with key components labelled

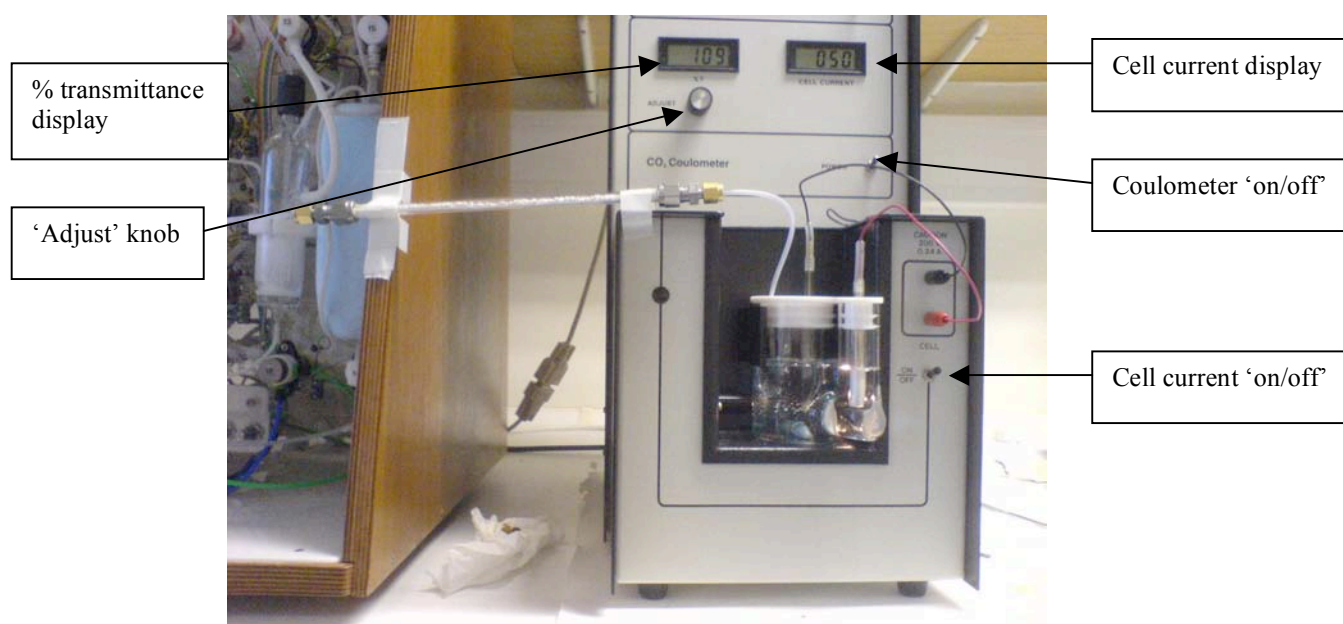


Figure 1.2 The UIC coulometer with coulometer cell in place

1.1. Preparing the equipment:

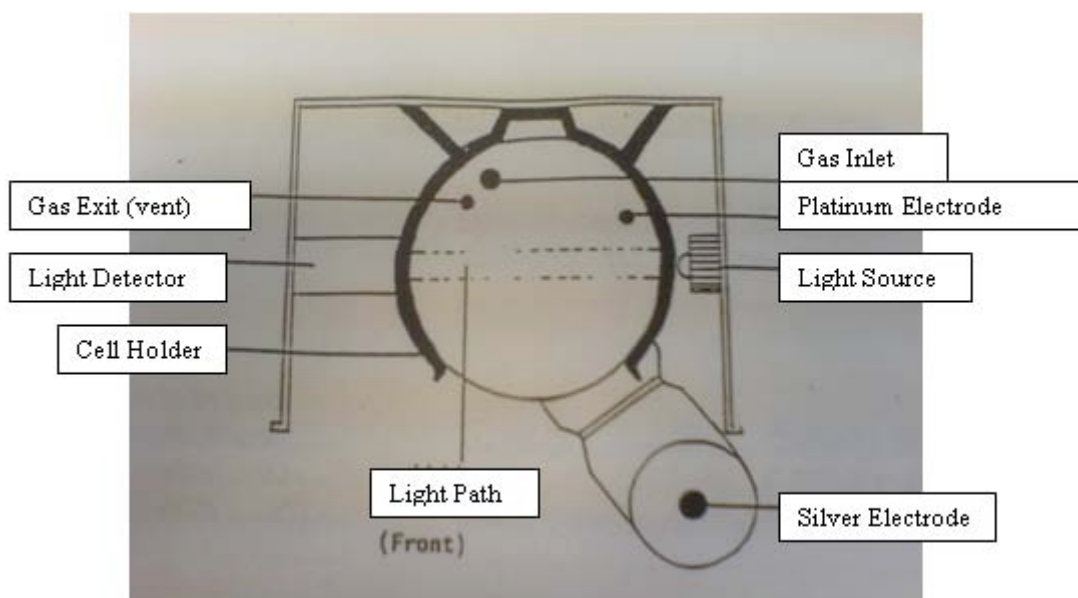
This routine is for starting the instrument from scratch or after it having been in hibernation. Photo guides to the VINDTA system are provided in the appendix.

- 1) Switch on the power to the Titrino, Coulometer and the water-bath at the plug. Turn on the water bath plus its cooling unit (2 separate switches), additional green power button on the upper part of the water bath may also need to be switched on with some models.
- 2) Once water is circulating turn on Peltier cooler at the top of the unit (this is a box towards the back of the instrument. The peltier cools the condenser to remove water from gas coming out of the stripper (Figure 1.1). Check the temperature occasionally as it cools. To do this, the digital thermometer display must be switched on to give a digital reading. The display unit runs on a battery so it must be switched off when not in use. The battery is a 9V square battery (there are spares). The temperature should go down to $<5^{\circ}\text{C}$.
- 3) The unit must be circulating for DIC analysis for the Peltier to work correctly. The water bath is set for 25°C . Put the CRM bottle in. The bath is filled with MQ water and 25% with methanol to keep it clean (2 ml Aquaclear may also be added to keep algae growth low).
- 4) Turn on Coulometer at socket and power switch (Figure 1.2). DO NOT turn on the cell current. The adjust knob should be turned fully clockwise on unit 011. On unit 024 press E enter.
- 5) Prepare coulometer cell. The cell has two chambers separated by a sintered glass frit: a large one for the cathode and a small one for the anode (ensure the cell is clean and dry before use).
 - Cathode (large cell) - Fill cathode cell with cathode fluid to the 100 ml line place a large clean magnetic stirrer bar in this cell
 - Anode (small) – Add anode solution to smaller cell to a level just below that of the cathode solution and add potassium iodide (KI) crystals (a small deposit at the bottom is enough).

The coulometer solutions come already prepared from the manufacturer, although there is a recipe for the solutions. This glassware should be cleaned very carefully after each use. **The glass coulometer cell costs £250, so take care when handling!**

- 6) Place the silver electrode in the small compartment (anode cell) and then fit the cathode lid and install cell into coulometer. The connections are slightly different for the two VINDTA systems. The lids are marked as 011 for the old unit and 024 for the new one. Check for any blockage in the carrier gas line between the condenser and the cell (using cat wire) then connect up the red and black leads, and the gas line to the condenser. Make sure that the magnetic stirrer controlling the flea is ON.
- 7) Place the cell so that the light path is unobstructed by the electrode, the anode rotated to the right in cell holder, and the gas line adjusted to point at back of cell (see Figure 1.3. Ensure the cell is aligned properly so as not to obstruct the light path through the large chamber of the coulometer cell.

Figure 1.3 Correct positioning of the coulometer cell (plan view).



- 8) Navigate the coulometer menu using the down arrow twice to navigate to 'prepare cell' and then press F2 when the reading is high (as prompted) but more importantly when stable. At the next menu select 'analysis' and switch on the coulometer cell. On VINDTA 11 turn on the cell current (eventually the coulometer will settle at 29% transmittance). The coulometer counter display will change rapidly until it settles down and the % transmittance meter stabilizes to read 29%. NOTE: If there is no display, press the reset button.
- 9) Prepare fresh 0.7M NaCl (4 litres) rinsing fluid every day. This is the solution that flushes the system between measurements. Prepare as two lots of 2 litres using volumetric flasks (2L = 81.966 g NaCl in MQ water).

- 10) Check level of 0.1M HCl titrant is over 100ml (prepared every 2-3 weeks using an ampoule of conc. HCl dissolved in NaCl, Appendix 1). When topping up the level it is best ensure this is carried out at the end of the day to avoid problems with bubbles, add a whole batch of acid at a time to avoid large shifts in CRM values. Each day bubbles are seen in the tubing, use the <DOS and <Fill keys on the Titrino to remove bubbles manually before turning the VINDTA PC program on. Occasional persistent bubbles can be removed by creating 1 large bubble (open the connector above the Titrino syringe on <Fill, remembering to close it again) to mop them up
- 11) Check level of 10% phosphoric acid in the 250 ml blue-capped bottle. Also check that the overflow level sensor is not screwed in too tight – the lid must also be free from moisture.
- 12) Check that the solutions in the AT electrode are up to the required level. The inner solution is 3 M KCl and the outer is 0.7 M NaCl. Expect a few mm drainage in the outer electrode, each day. The filler ports for the solutions are covered by white silicon rubber flaps which are left open when titrating. Never let the electrode dry out and always use plastic pipettes to introduce the solutions. Remember to close the flaps at the end of the day.
- 13) Check that the walls of the soft tubing are not stuck (especially valves 13 and 14 – do not move the tubing from other valves, especially around the volume calibrated pipettes) Slide the tube out of the valve and gently roll it between the fingers to open it fully. It may be necessary to repeat this procedure during the run if problems occur with the gas flow.
- 14) Check Peltier cooler is at correct temperature (below 5°C and ideally between 1 and 2°C). The condenser will also feel cold.
- 15) Turn the VINDTA PC program on (see software set-up below), note that if the software is not on, the gas will not go through and there will be no bubbling.
- 16) Turn on the nitrogen carrier gas supply and adjust the pressure to 1.5 bar. Bubbling should start in the stripper and the cathode chamber of the coulometer. If this bubbling is not seen, there is possibly a blockage in the scrubber or in the cathode inlet tubing or the software has not recognized the gas (if so then adjust the yellow 'set flow' to 149 ml/min). If gas pressure is too high, the tubing will pop off. If so then adjust to 1bar at the regulator.
- 15) Close the gates in the peristaltic pumps so that the tubing is compressed and the pumps will function. These gates are left open when the system is not in use to stop the tubing from being pinched closed.
- 16) Run Junk samples while the unit stabilises for at least ½ hour.

- 17) Always leave the stirrer on the “on” position. It will stop automatically on Vindta24 when the program is off (note there is a small switch at the back of the control board).
- 18) Each day select ‘kill cell’ and ‘new cell’ to add the anode and cathode lot numbers.

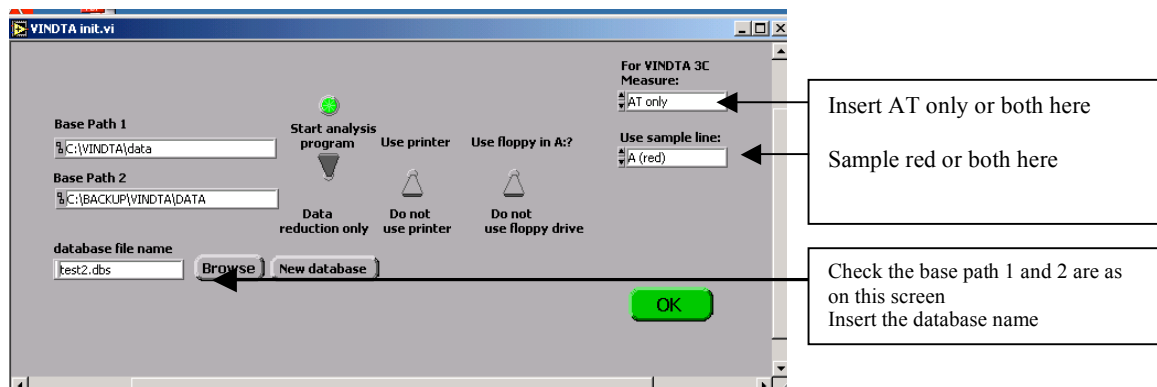
1.2. Software start-up

Turn on the computer and start up the VINDTA software. Username for the 011 computer is Administrator; Password is ‘admin’ (case sensitive). The VINDTA system is controlled by VINDTA reduction software (VINDTA011.exe, ‘+’ icon on desktop).

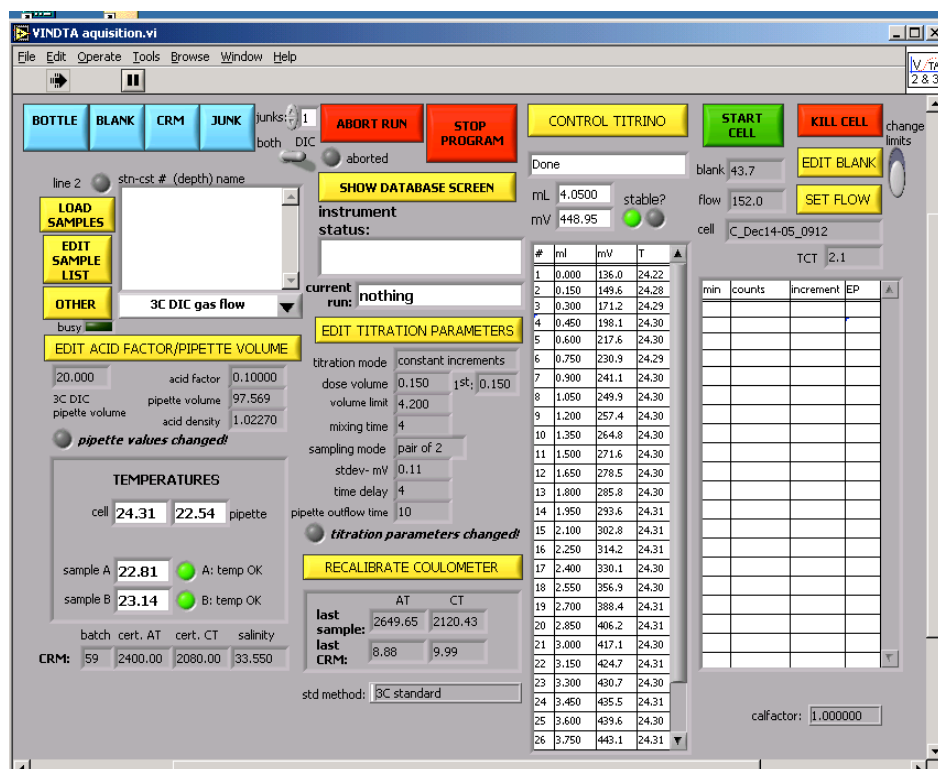
Important note:

If you wish to exit at any stage the windows must be closed by following the exit procedures – do not on any account use the cross at the top right of the window as the program will still try to run in the background.

- 1) Click on the desktop icon for VINDTA011.exe (or VINDTA024.exe for the newer VINDTA system).
- 2) Select a log file at the next screen (CTD merge storage. log) and SAVE as prompted then confirm that it is the Southampton system on the next 2 screens as prompted.
- 3) Select ‘**configuration**’ (yellow box) program to perform hardware check on the electrode, select ‘check EMF electrode’ (stdev should be lower than 0.09 mV). If there is a drift at the start of the day then it may need the electrode solutions changing or it may be due to HCl in the solution (eg: if DOS key has been pressed at the start of the day to clear bubbles. Press the button STOP to quit. Note that at the ‘configuration’ stage new pipette volumes can be added if they have been recalibrated.
- 4) Select ‘Start measurements’; this opens the VINDTA.init.vi page and this is your opportunity to make sure the database is correct. For continuity use the previous database (or create a new one E.g. trial.dbs).
- 5) Select to run DIC and AT together (they could also be run separately). Select sample line A (red), then press “OK”. **In theory the system can use 2 sample lines (to lengthen time between sample changes to 40 minutes), however it will not operate with yellow line alone.** There are problems with this option as the first reading is not recorded.



- 6) A new page will come up 'Please wait while system initialises'.
- 7) The next screen to appear is the VINDTA acquisition.vi screen. This is where the sample details will be introduced and the system is controlled.

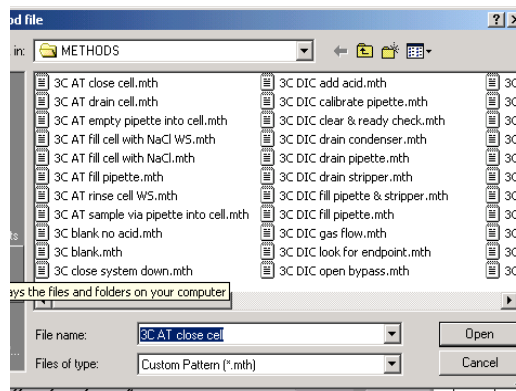


Use the red KILL CELL button (top right of screen) to kill the Cell and the Start a new cell. This allows the TCT (Total Carbon Titrated) to be monitored by resetting it each time. Insert the cathode and anode solution batch numbers as prompted. Select the yellow 'set flow' to reduce the gas flow to 149 ml/min (from 150). This will start the gas flowing in the stripper and the cell if this has not happened automatically at this point.

To run individual parts of the system click on the down arrow (see above) to open the pull down menu of choices and click on the one you require. This drop down menu panel

allows you to intervene in the process and instruct the machine to perform various individual functions e.g. AT empty pipette into cell, AT fill pipette, draining the condenser, DIC drain condenser, DIC drain stripper etc. If there is a choice, use the AT commands ending in WS (i.e. with sensor) since there is now a level sensor in the titration cell.

Then click the **OTHER** box and the method file will come up as a check



Click on open and the program chosen will run

NOTE: To close the program at any time, use the exit procedure rather than just clicking on the cross box because otherwise the program will still be running in the background.

Use the STOP PROGRAM and EXIT commands on each of the program windows to stop and then use the highlighted cross on the top right corner.

The codes for each individual method can be viewed from 'My computer'. The methods are stored under C:\VINDTA\LABVIEW\VINDTAgeneral\utilities\METHODS

The following methods are useful to run at the start of the day:

- a) '3C check all of the valves'
- b) '3C DIC gas flow' to check the flow is at 150 ml/min (± 2 ml/min)

A note on the gas flow: If the flow is less than 150 ml/min it is likely there is a block or a leak in the system (see troubleshooting). When the system is not in use (e.g. over lunch), reduce the gas flow to a minimum using the "SET FLOW" button on the right side of the VINDTA acquisition window. This reduces the flow from 150 ml/min to 10 ml/min. When ready to start measurements again, remember to return the flow to 150 ml/min.

The following programs can be used if the system has been off for a while, although the Junk routines do this anyway:

- d) '3C DIC fill pipette and stripper' fills small pipette then drains it into stripper
- e) '3C AT fill pipette' fills alkalinity (large) pipette
- f) '3C DIC drain stripper' Empty out the stripper
- g) '3C AT drain pipette' Drain alkalinity pipette in titration cell
- h) '3C AT drain cell' Drain titration cell

Each day run the following:

1 Junk

3-5 sub standards

Blank measurement

CRM1 record on graph (replace stopper then return to water bath ½ hour before running again ½ way through the run)

Samples x20

CRM2 (sample bottle as CRM1)

Correct all sample using correction coefficient in the Excel spreadsheet (based on certified value of CRM).

1.3. Running Junks

Junks are run each day to get carbon through the cell. This is then followed by at least 3 sub-standards, the blank and then the CRM. **Note that for Junk samples there is no end point and results are not stored.** Running 'junk' samples is a useful test of the system and useful for flushing the system out if it has been left for a few days.

Run a junk sample = 'junk' (blue) key on the VINDTA acquisition.vi screen. Select the "switch" icon for just DIC measurement. Place the red inlet tubing in a beaker of sub-standard on the bench. It does not have to be equilibrated to 25°C. You will need to add the DIC only method '<3C standard DIC only' on the old 011 VINDTA unit when prompted (this is found automatically on the 024 unit).

For the first junk measurement of the day, the blank used for the DIC measurement will be the one from the previous time. As with all DIC measurements made the increments between readings get smaller and the final increment approaches zero. The later increment represents the likely blank value as nearly all the DIC has reacted with the acid.

1.4. Running sub-standards

The first sub-standards run through the VINDTA each day are effectively ‘Junk’ samples with the results recorded. It is best to edit the blank to a high value (200) in order to pass the ‘clear and ready check’. Remember to reset the blank later.

Sub-standards are also used to calculate precision running at least 3, preferably 5, sub-standard samples through the instrument as ‘samples’ (as opposed to ‘junks’). Use the same water for all your sub-standards (bulk, HgCl_2 preserved seawater is decanted into bottles from a bulk supply when available). The first two will flush the system and the next 3 are for the consistency check. If measurements are continued for a number of days, do 3 sub-standard measurements at the start of each day to check consistency.

The first 3 sub-standards should have been in the water bath for >30 min so that they are equilibrated to 25°C. Remove the glass stopper from the first one and put the red sample inlet pipe into the bottle. It should rest in the mouth of the bottle so that the sampling inlet is about $\frac{2}{3}$ to $\frac{3}{4}$ the way down the bottle. Enter the name of this sample relating it to the data (as the db file does not record date so this is a useful way to track analysis dates). Select 'edit sample list' (the yellow button) and the following VINDTA sample list.vi will open the date and identifier into the 'bottle' part of the sample list.

[illegible]

Select 'Add sample to list' – this allows you to add information about the samples

In the bottle column fill in the sample name e.g. 141106sub 1

Select the green 'DONE' button and the bottle name appears in the VINDTA acquisition.vi window

To run the sub-standard, select the name of the bottle by highlighting it in the list (from Vindta acquisition.vi window). Select the blue 'BOTTLE' button and select the method as prompted.

>3C Standard >OPEN

Select the file for the titration data e.g. 141106sub_1

>SAVE - the sampling process will then start, the red busy light goes ON and the counter starts.

When all samples are run, precision should be calculated by:

Precision = Standard deviation of sub-standards

This should be lower than 2 $\mu\text{mol/kg}$ (0.1%) for both AT and DIC. If precision is $>2 \mu\text{mol/kg}$ see Troubleshooting (Appendix Section A5).

For the Sub-standards collect 8 litres of low nutrient open ocean sample, filling a 10 l plastic bottle using a measuring cylinder adding HgCl_2 at 200 μl stock (7%) per litre i.e. 1.6 ml in 8 litres. NOTE: wear gloves when handling HgCl_2 stock.

1.5. Checking the blank

- The blank is used in the calculation of the result, therefore the lower it is, the better. The blank is determined using the method file 3C blank. Do not click the BLANK button in order to run a blank, as the program will not stop and will automatically run another blank. Use '3C blank' from the drop down method menu and press 'other'.
- The system is run without any sample added. Phosphoric acid is added to the empty stripper. Repeat this every time you start the machine or after every 8-10h of use. The system will run without adding sample giving counts and increment. The final count is a mean of 10 readings taken over 10 minutes. If the first few readings are high i.e. >400 , it is obvious that the final value will be >150 and the system will automatically repeat the process. To avoid wasting time, ABORT the BLANK process and start again. However do not use ABORT frequently unless you have a big problem (ie:

water coming from everywhere, etc...). But if you do use it you need to drain the stripper before trying again:

>3C DIC Drain stripper (to assist draining, make sure that the stripper is vertical).

The coulometer blank is ideally between 40-70 but can be run up to 150. Low blanks mean that the 'clear and ready' check takes longer to complete or no endpoint can be reached so it is wise to 'edit blank' (in the vindta.acquisition.vi screen) to be 10-20 units higher than the reading. It may be necessary to repeat this procedure 4-5 times to get an acceptable BLANK value i.e. ≤ 100 . If the blank is greater than 150 you cannot continue, refer to Troubleshooting in the Appendix. Remember to drain the stripper after running the blank.

1.6. Assessing Accuracy Using Certified Reference Material (CRM) seawater samples

When precision is $< 2 \mu\text{mol/kg}$ and the blank has been set, a Certified Reference Material (CRM) sample should be run to check accuracy and calculate a correction factor for the results. A new correction factor should be derived for every 20 samples analyzed (a fresh bottle daily). The CRM samples are sealed bottles of seawater with certified levels of AT, DIC and other components (stored in the labeled grey crate in the CO₂ laboratory). The certified values for DIC and AT result from highly accurate measurement by A. Dickson (Scripps's Oceanographic Institute, USA). Certified values can be found at <http://andrew.ucsd.edu/co2qc/batches.html>.

Bring an unopened bottle to temperature in the water bath, noting the bottle number eg: 091-640 (batch 91 bottle 640). The CRMs have ground glass stoppers, held on by black tape and sealed with grease which can be quite difficult to remove. Once up to temperature, insert the sample line ensuring it does not go further than half way into the bottle (this is to avoid problems with repeatability). If the CRM is too cold, replace the stopper.

Run a Certified Reference Material sample by pressing the blue 'CRM' button to the top left of the acquisition.vi screen (**not the 'sample' button**). A screen will appear in which details of the CRM sample can be entered. This shows all the previous CRM batches used for calibration with all the measured parameters. Choose the corresponding batch from the menu if the details are already entered. If it is a new batch, create new batch and enter corresponding certified values. Enter bottle number (found on the left side of the sticker on

the CRM bottle) then select: OK>OPEN>SAVE (edit the file name to the batch and bottle number as follows eg: 91-0 340 (0)1)

Once the CRM has run, record the measured results ('last CRM' on the acquisition.vi window) and calculate the up-to-date correction factor by:

$$\text{Correction factor} = \text{CRM value} \div \text{VINDTA value (TA or DIC)}$$

The resulting correction factors for AT and DIC should be applied to any sample measurements as follows:

$$\text{Final result} = \text{VINDTA result} \times \text{Correction Factor}$$

Use the same CRM bottle at the end of the day as this is just to check instrument drift.

Change the file name to reflect duplicates eg: using 91-0 340 (0)2

When you are finished with the CRM bottle you've been using, empty the bottle of remaining water into the 'poisoned sub-standard container (as it is spiked with HgCl₂) and wipe off the grease from the stopper. Rinse the bottle with hot water and put back in the CRM crate so they are ready to send back to SCRIPPS.

The CRM values should be put onto a control chart. This charts the mean (of at least 10 CRM readings) the 1, 2 and 3 SD.

2. Running DIC and AT samples

- 1) Samples should be at 25°C ($\pm 0.3^\circ\text{C}$) before being run through the VINDTA instrument.
- 2) Click on the yellow 'edit sample list' and the following screen appears VINDTA sample list.viz

The screenshot shows the 'VINDTA sample list.viz' window. It features a menu bar (File, Edit, Operate, Tools, Browse, Window, Help) and a toolbar with icons for file operations. Below the toolbar is a 'Sample list' table with columns: Type, Bottle, Stn, Cast, Niskin, Depth, latitude, longitude, salinity, temperature, phosphate, and silicate. The table is currently empty. Below the table are input fields for Latitude, Longitude, Station, Cast, Niskin, Depth, and Bottle. There are also radio buttons for 'Decimal Degrees' and 'Degrees-Minutes'. A summary box on the right shows 'salinity' (not known, 35 default) with a value of 35.000, 'temperature' (not known), and 'nutrients' (not measured, 0 default). At the bottom right are 'Add Sample to List' and 'DONE' buttons.

- 3) Enter samples details. Add ID of the bottle to the 'Bottle' box, and relevant details of *in-situ* sampling. If you don't know the salinity yet, use default of 35. Click on 'Add to sample list' then 'Done'. It will be saved as a database file in c:\VINDTA\data.

A note on naming samples: For example sample 84 from May 2007 the file name should be "0705-0 084 (0)1". Avoid the use of dots – eg: a decimal jday will be ignored and only the integer digits will be recognized.

- 4) Leave the bottle in water bath for at least ½ hour before opening. When opened, wipe the red sample line with tissue. When ready, insert sample line so it doesn't go more than ¾ way to the bottom of the bottle
- 5) On the VINDTA acquisition.vi screen you should now see the bottle names in the window. Click on the one you wish to titrate and click on **BOTTLE (Blue button)**.

A warning that the temperature is too low may come up and you can choose to ignore this (although this is not recommended). If too cold, replace glass stopper to avoid atmospheric exchange

6) Click 'Bottle' and select method "3C standard " for both alkalinity and DIC

7) The next window is the data file, which now needs to be saved. If no 'cast number' and 'depth' are entered in the data window it is recommended to delete the zero's that appear before the filename before saving. Sometimes the name in use already exists and you will be prompted to enter a new name (if this happens at the end of analysis it means overwriting the data file which makes recalculation difficult).

8) The titration will begin and values will be recorded in the columns as it proceeds.

9) The number of 'counts' are recorded for each sample in the Logfile.bak. These counts appear every minute of titration in the right hand section of columns in the 'acquisition.vi' screen. These counts can be used later to perform corrections. It takes >1300 seconds to run a DIC plus AT sample. Have the next sample ready to run once the progress of the DIC and then the AT titrations scroll onto the screen.

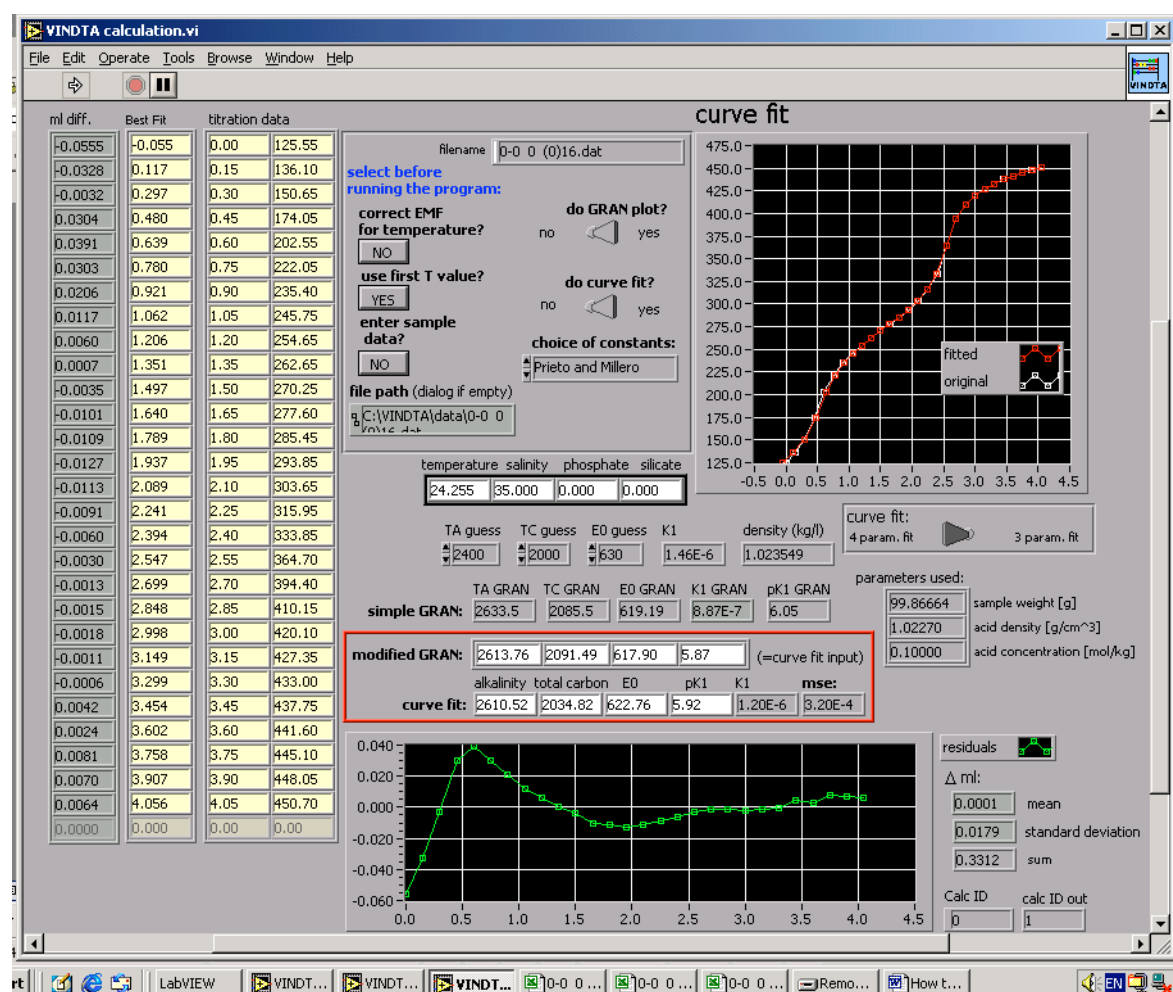
10) sub sample for nutrients (into clean 20 ml diluvials – and place samples in the fridge 11) Put remaining sample into the waste containers (if HgCl_2 poisoned) and wash the bottles up a few at a time in hot water (removing all labels) and rinse in MQ water. When drained and dry replace the stopper (using paper to stop the stopper from getting stuck).

3. Calculating results

The logbook is invaluable for tracing sample details and results. Historical data will be in various laboratory notebooks, different *.dbs files and have various methods for assigning sample names (although from 20/1/09 the nutrient number has been used as a unique number within the name). Results for both AT and **DIC** are stored in the 'reduction.vi' screen which is the *.dbs file. Results are appended for each run.

The 'Calculation.vi' screen comes up briefly at the end of each run but only lasts 2 seconds after the titration has been carried out. However this calculation screen can be retrieved to view the AT titration details through:

VINDTA\VINDTA General\Labview\calculation\VINDTA calculation.vi



Each sample has a separate raw data file (*.dat) for alkalinity. These are used in Matlab processing of the results, alongside all collated data (including salinity and nutrients when available). The 'logfile.bak' is an appended file of DIC raw data.

The following procedures should be followed on each day of analysis to record data.

- 1) Data output is put into a worksheet within an Excel spreadsheet kept locally on the laboratory PC. The spreadsheet is of the form 'raw data start date-end date'. The initial AT and DIC results are recorded – there are further columns to account for the CRM. Following Matlab processing at a later date there will be columns for 'TA Matlab' and 'TA Matlab CRM corrected', which will go back into the raw data Excel file for traceability.
- 2) All CRM results (from the start and end of the analytical run) are put into this spreadsheet, the correction factor that is applied to all samples is based on the difference between the measured and certified value. It is possible that a daily CRM correction adds to variability in the data due to individual bottle contamination (A.Dickson, pers.com).
- 3) The Excel sheet also contains the sub-standards run for each day. These should be entered into the VINDTA in the form of 'SUB1 date' (eg: with date in the form of 090502 for the 2nd of May). This will help to distinguish each run and make tracing back to the laboratory note book an easier task as the date of sample analysis is not recorded in the appended *.dbs file.
- 4) List all values, including CRMs and record any problems encountered into the Excel sheet and the Logbook. Data since 28th October 2008 has also been collated into one Excel file ('Vindta data Oct 08 to end date'). This will include all precision, CRM, Matlab and raw data along with comments and quality flags. This will also include all salinity measurements and nutrient concentrations (from samples at source in the case of PoB and on sub samples of the DIC/TA sample for all other samples)

Results can be retrieved from the VINDTA reduction.vi screen, which lists DIC (as CT = total carbonate) and alkalinity (as AT). You can also record the results as they appear on the VINDTA acquisition.vi screen.

3.1. Running Matlab to process samples

Matlab routines are run to correct the alkalinity for salinity, nutrients and the acid factor (acid concentration, density and sample pipette volume are in a small text file used in

the processing). The results generated by Matlab processing will still need to go through Excel to apply the new CRM correction factor (the CRM will also change through the Matlab processing). The Matlab program requires a template (recording the year, month, 3 digits sample or Niskin number, raw AT value, salinity and nutrient data). The sample number (also year and month) must match up with the name of the *.dat file.

Eg: File 90-0 574 (0)1.dat is for CRM batch 90 and bottle 574. For sample 84 from May 2007 the file name will be:

0705-0 084(0)1.dat.

The flowchart in Appendix 6.8 describes the steps and necessary files. The required folder: S:\OBE\Ferrybox\POBmatlab

The folder includes:

1) The template (see Appendix 11) to set up the samples - save it as a text file in this location eg: TAlk_POB_allruns:

S:\OBE\ferrybox\POB matlab\POB

The .dbr file (from the Vindta PC) gives the list of all the samples analyzed. In the template put samples in the same order as in the .dbr file.

2) The acid file: TAlk_POB_Acidlog (Appendix 11) must be edited to take account of any changes in pipette volumes. Note that the pipette volume is 95.023 ml from 3/6/09 for VINDTA 11. Prior to this the pipette volume was 97.577 ml and was changed to 94.939ml in August 2010. . On the new VINDTA (024) the pipette volume is significantly different and the Acid log file will need to be edited to account for the new volume (105.043 ml). The acid factor was change on VINDTA 24 on the 17th Aug 2009 (to 0.0878) so that the VINDTA TA output approached the certified TA value for the CRM. However in the acidlog file the concentration is 0.099 mol/kg and the density 1.0227 kg/l (for this reason the matlab CRM results will differ from VINDTA CRM output).

3) Copy all the *.dat and the dbr files from the computer attached to the VINDTA. You can find them in:

C:\VINDTA\data\your_folder (copy the folder discarding .c01 files.)

Copy the DAT files, with all AT titration raw data, into this directory: S:\OBE\Ferrybox\POB matlab\POB\Titration_data. You will have to change a few things in

Matlab as the names of your folders might differ (Appendix 11), but this is relatively easy (change the folder name for the *.dat files and the name of the new results file, the name of your template file and the year eg:07, 08). Run the Matlab program (**calcalk_allruns.m**) and it will send the recalculated results as a text file in this directory:

S:\OBE\Ferrybox\POB matlab\POB\Titration_results.

Copy an excel file in the directory to get the first row corresponding to each column as these titles are not produced by Matlab. You need the MLSQ alkalinity result. Copy and paste these values back into your Excel file using the raw AT value to track the results. Make sure that the initial AT values and the CRM initial AT corrected values are copied into neighboring columns for traceability of the data. Note that the CRM will also change with Matlab processing and this will need to be added to the Excel file too (keeping a copy of the initial values again for traceability). The Matlab program is from UEA and the output differs slightly (within 1 $\mu\text{mol/kg}$) to the output from a program supplied by Steven van Heuven (the advantage of his method however is a PDF file that shows the acidlog parameters that have been used).

The DIC data (CRM corrected) need to be further corrected for density changes once salinity is known.

3.2. *CO2 SYS program to calculate other carbonate variables*

- Download the program at this address:

http://cdiac.ornl.gov/ftp/co2sys/co2sys_xls_program/

Choose the CO2sys macro .xls file (for MAC or PC depending on what you're using)

- Open the file on your computer

- Check macros are enabled on your computer

- On the Input spreadsheet you can select which pH scale and which set of constants you want to use (the recommended ones are the Total Scale and the Mehrbach et al. 1973 constants as well as the Dickson KHSO_4 constant)

- On the Data spreadsheet, you just have to enter your data as specified.

For the input data you have to give the temperature measurement (i.e. 25), the laboratory pressure (i.e. 0), but also the in-situ salinity and nutrients data. If you do not have the nutrient data for some samples, just leave the cell blank. The program will still do the calculation.

The output conditions are the other in-situ parameters: temperature in-situ and pressure for the sampling.

Next to it you have to enter your data: Total Alkalinity (recalculated with Matlab and CRM corrected), and then DIC (TCO₂) also CRM corrected.

- Press the red START at the top of the spreadsheet and click YES twice. Your results will be located on the right of the spreadsheet in the RESULTS (output conditions) section.
- You can also find all the information about how to set up your data on the INFO spreadsheet in the same file.

4. Vindta shut down procedure

4.1. Daily shutdown

This procedure is recommended for daily shut-down of the system when sampling is expected to resume within 3-4 days. The order of this procedure is important and should be followed as below:

- 1) Undo the clips compressing the tubing in the two peristaltic pumps to prevent the tubing from becoming pinched.
- 2) Turn off the cell current on the coulometer. Disconnect the electrode leads
- 3) Turn off power to coulometer on the unit and at the plug
- 4) Turn off gas supply using the gas spanner;
- 5) Turn off Peltier cooler ALWAYS before turning off water bath
- 6) Turn off cooler unit of waterbath (lower switch)

Check level of waterbath (top up if low) and place cover on Turn off the cooling unit of the waterbath (bottom switch); if this is not done and the level of waterbath drops below the circulation pump then the waterbath will freeze solid. Likewise it will freeze if the float is not free to move (so always ensure samples are kept away from the back of the water bath tank.

- 7) Empty coulometer cell into organic waster container

Remove cathode cover but leave anode cover on

Pour contents of cathode cell into container, rinse out with MQ water

Remove anode cover, pour contents into container, and rinse out with Milli-Q water

Rinse electrodes in Milli-Q (the platinum electrode should be dipped into nitric acid for 10 seconds the MQ rinse). Clear the tube out with wire (the cell inlet tube has been cut to minimise the buildup of precipitate)

- 8) Wash cell thoroughly with de-ionised water (use gloved fingers to clean the frit). Pull 25ml of DI water through the frit - use the vacuum pump for this. Occasionally follow this with methanol to clean the sintered glass frit separating the cathode and anode chambers. Polish the glass (not the frit) dry with clean blue tissue to remove any dye that has stained the glass. If the sintered glass frit between the cells becomes coloured, rinse with 1:1 nitric acid (left

overnight) and then wash extensively in milliQ. If the potassium iodide turns brown after filling the anode compartment the cell has not be sufficiently rinsed.

9) Close the software and turn off the computer.

10) Close reference electrode reservoirs

11) Refill the bottle of 0.7 M NaCl, prepare more sub-standard and replenish the acids if necessary.

12) Fill in the log book with samples run and lot no. of chemicals used.

13) Empty the drain waste into 25L containers for collection by NOC facilities (marking the collection sheet as 0.0007% Mercuric chloride in seawater).

Note: for collection of organic coulometer cell waste phone reception for large white containers, place organic waste bottles directly into this for collection marking the content sheet as: DMSO, ethanolamine, potassium iodide and thymol blue

4.2. *Extended shutdown ('hibernation')*

If the instrument is not going to be again within a month then further procedures should be followed as well as the above. Replace phosphoric acid bottle with Milli-Q water. Empty waterbath and circulation system of the VINDTA instrument

Rinse all tubes and pipettes in MQ water and leave the titration cell filled with 0.7M NaCl. Ensure the stripper is empty. The AT electrodes should be placed in their protective sleeves, located on the small rack to the left of the titration cell. All the units, including the Titrino and waterbath should be turned off

5. *Maintenance*

- Need a fresh coulometer cell and solutions each day or every 70 hours (or 60 samples) if run continuously. Note that it takes about 1 hour to stabilise a new cell.
- Change the tubing twice a year.
- Clean all glassware thoroughly; use a nitric acid bath once a year. If the coulometer frit becomes blocked (a general indicator is the cathode solution won't turn blue), clean with 50% nitric acid.
- Clean the Pt electrode with nitric acid.
- The pipette volume calibrations should be checked periodically (see Appendix 2)
- The temperature sensor calibration should be checked twice a year (see Appendix 3)

6. Appendix

6.1. Preparation of chemicals

Read all COSHH forms. The samples are poisoned with mercuric chloride, which has associated medical and environmental hazards that must be considered. The procedures also include the use of organic chemicals and caustic chemicals such as HCl acid.

1) 0.1 M HCl – used as a titrant in the Titrino burette, this needs to be fortified to the ionic strength of seawater to avoid problems with density gradients. Preparation guidelines for 500 ml of the acid solution are as follows:

- Rinse the contents of 1 Merck titrosol 0.1M acid ampoule into a 500 ml volumetric flask using Milli-Q water (~100 ml). Follow the rinsing guidelines given on the ampoule.
- Dissolve 35.086 g of analytical grade NaCl into ~150 ml of Milli-Q in a clean 500 ml measuring beaker.
- Add the dissolved NaCl to the volumetric flask.
- Use ~200 ml of Milli-Q water to rinse any remaining NaCl from measuring beaker into volumetric flask.
- Fill volumetric flask to 500 ml line using Milli-Q water.
- Fit stopper to volumetric flask and shake repeatedly to dissolve contents.
- Add the contents of the volumetric flask to the HCl bottle of the Titrino unit.

2) 0.7 M NaCl – used as the outer electrode solution and in the main Titrino cell (it becomes acidified as the Titrino is run through). Prepare 2 litres as follows:

- Weigh 81.966 g of analytical grade NaCl into a clean 500 ml measuring beaker
- Add ~300 ml of Milli-Q water to the NaCl and stir to aid dissolution
- Add the contents to a clean 2000 ml volumetric flask
- Using ~200 ml of Milli-Q water, rinse measuring beaker into volumetric flask
- Repeat the last step twice more to ensure all NaCl is added to the flask
- Fill volumetric flask to 2000 ml line with Milli-Q water
- Fit stopper to the flask and shake repeatedly to dissolve the NaCl
- Add the NaCl solution to the rinsing fluid carboy at the left hand side of VINDTA
- You can choose to keep a small amount to add to the titration electrode

3) 3 M KCl – used as the inner electrode solution- 22.368 g per 100 ml deionised water

4) 10% phosphoric acid – used in the bottle with the blue lid, dispensed into the stripper.

Dilute phosphoric acid with Milli-Q water to 10% strength.

5) Anode solution (Dimethylsulphoxide and KI) – used in the small arm of coulometer cell

6) Cathode solution (ethanolamine, tetraethylamoniumbromide and thymol blue indicator solution) – used in the large part of the coulometer cell.

Coulometer solutions (acquire pre-prepared from RS Slaughter but can be made up to a recipe if required): Anode – 400 g KI, 480 ml DI water, made up to 4 L with DMSO

(dimethylsulfoxide). Cathode – 1 L ethanolamine, 1 L DI water, 400 g

tetraethylamoniumbromide, 53 ml indicator solution made up to 20 L with DMSO. Note that the indicator solution is 265 mg thymolphthaleine in 100 ml DMSO.

7) Potassium iodide (KI) use AR grade - add 2 full spatulas to the anode solution as an indicator

8) N₂ carrier gas

Contact reception if the supply runs out. Always use a gas cylinder carrier (with a chain) and keep the cylinder attached to the bench in the laboratory. The gas should last for about 2 months, if it runs down faster than this then there may be a problem with the cylinder, regulator or there may be a leak in the tubing. Gas is kept in the outside gas cages.

Information on VINDTA stocks can be found on the shared drive. Under NMFD select Logistic Services and then Gas.xls. Ensure that the gas regulator is switched off each night (using just the gas spanner to avoid over tightening of any connectors).

6.2. Calibrating the pipettes

For calibration of both the AT and DIC pipette use the glass and plastic bottles stored on the shelves across from the VINDTA 024 instrument. The file used for calibration calculations can be found on the desktop of the VINDTA 011 PC 'calibration_pipette.xls', use the pipette_calibration worksheet as in the example below.

bottle	Weight Empty (g)	date	T [C°]	Pressure (mbar)	Humidity (%rel.)	Air density	Weight corr.
--------	------------------	------	--------	-----------------	------------------	-------------	--------------

						(kg/m ³)	(g)
1	48.4789	08/02/2000	16	1014	57	0.0012173	48.4984
2	47.74824	08/02/2000	16	1014	57	0.0012173	47.7674
3	48.33406	08/02/2000	16	1014	57	0.0012173	48.3535
4	47.87164	08/02/2000	16	1014	57	0.0012173	47.8909
5	47.8408	08/02/2000	16	1014	57	0.0012173	47.8600
6	47.8408	08/02/2000	16	1014	57	0.0012173	47.8600

	difference			volume		
	[g]	± [g]	± [%]	[ml]	± [ml]	± [%]
average:	98.6024	0.0273	0.028	98.895	0.027	0.028

Put the new values in the 'calibration' tab at the Configuration stage of Vindta startup.

For AT pipette

Weigh each of the 5 labelled plastic bottles (ensuring they are clean and dry)

Fill the large pipette with deionised water using the '3C fill AT pipette' command

Remove the tube leading from valve 3 from the titration cell, and place it in Bottle A

Select the '3C drain AT pipette' command

The large pipette should drain into the plastic bottle

Repeat for bottles B-E

Weigh the full bottles and enter all the values plus date, air pressure and humidity (use the BBC website) into the calibration spreadsheet stored on the laboratory PC. The pipette volume will need to be changed under the configuration page of the software and a note made to change the Acid log file.

For DIC pipette

Weigh each of the five small glass bottles (ensuring they are clean and dry)

Fill the small DIC pipette with deionised water using '3C fill DIC pipette'

Remove the tube leading from valve 10 from the stripper and place in Bottle A (see Figure A2 in Appendix)

Ensure the gas flow is turned on as this is required to help purge the water out of the DIC pipette. Select the '3C empty DIC pipette into stripper' command'

The DIC pipette should drain into the plastic bottle

Repeat for bottles B-E

Weigh the full bottles and enter all the values plus date, air pressure and humidity (use the BBC website) into the calibration spreadsheet. The pipette will need to be changed under the configuration page of the software and a note made to change the Acid log file at the Matlab processing stage.

6.3. *Temperature sensor calibration*

Place the sample and TA cell temperature probes into a second water bath. Use a tray or foam to make sure the sensors are not touching the side of the bath. Use a 2nd temperature probe to confirm the temperature of the bath. Set the water bath to 10 degrees (press 'T' then use the arrows on the water bath controller, select the final temperature using the bottom right arrow). Open LJStream and the voltage outputs are seen on the screen (A=sample1; B=sample 2' C=TA cell) When the reading is stable enable 'write to file' and record the output for about 3 minutes then open the file created (data1) in Excel and average the voltage readings for each column Repeat this process with 5 degrees increments up to 30 degrees then reverse back down to 10 degrees. The temperature at each point should then be plotted against the averaged reading and slope and intercept of the line obtained. Put these values into the calibration page on 'configuration' at the point when the VINDTA software starts up. Monitor the cell temperature as variability may arise due to blockages in the water flow from the heat bath.

6.4. *Preparing the scrubbing cells*

The scrubber removes all CO₂ from the N₂ gas. It is composed of two layers separated by glass wool. The top is magnesium perchlorate and the bottom is soda lime. Signs indicating that the scrubber needs changing are if: There is condensation visible in it or there is poor stability of the coulometer and the BLANK value remains too high. To be on the safe side, change the scrubber after every week of use. The scrubbing cell at the entrance to the VINDTA should be in place at all times. If they are broken, dislodged or contaminated (most likely moisture) then follow the guidelines below to prepare fresh cells:

1. The scrubbing cell should be clean and dry
2. Prepare magnesium perchlorate by placing in between a folded piece of A4 paper and 'cracking'- i.e. applying a swift impact to the crystals. It is important they are

‘cracked’ and not ground otherwise too much powder is created and the cell will become blocked.

3. Place a small piece of rolled lab tissue in one end of the scrubber cell
4. Using the A4 paper as a funnel, pour the prepared magnesium perchlorate into the cell
5. Fill to $\frac{1}{2}$ level, and then insert another rolled piece of lab tissue into open end of cell. Fill the rest with soda lime.
6. When shaken, contents should settle throughout cell whilst leaving enough room for gas flow to pass through.
7. Re-attach to gas line, use Snoop® to check for leaks.

6.5. Troubleshooting and "top tips"

Slow TA titration

This may be down to the electrode solution: If the titration times are long change the inner solution (3M KCl) as crystals may form at the bottom of the reservoir. Make sure to dissolve all the crystals (this can be done with milli-Q water), and refill the reservoir with fresh KCl solution. The outer electrode reservoir, (filled with 0.7M NaCl, as used for flushing the cell), should drain slowly by about 3-5 mm within 24 hours (so refill daily). If the level is not sinking at all, get suspicious. Every one or two weeks, empty both inner and outer reservoir, check electrode end bulb is free to rotate but is not leaking and fill it again. Never let the electrode dry out and always use separate plastic pipettes to fill the reservoirs. Close the reference electrode reservoirs at the end of the day to prevent the liquid levels draining. Also check that the stir bar is spinning in the TA cell – sometimes the stir bar gets stuck at the temperature probe. When switching between Metrohm Titrino units the correct stirrer lead must be used otherwise there will be variable stirring in the cell which can also slow the titration down.

Cell level error

Check that the sample is going into the pipettes and that NaCl wash is going into the cell. If there are kinks in the tubes or the peristaltic pumps are not free to rotate (check to see if the pump works when the pump platen is loosened) and also to see if the pump is getting hot. Ensure that the top of the level sensor (at pipette overflow) is not done up too tight, and that the lid is clear of moisture.

Noise

The system might be too noisy (this means that the system probably won't get values lower than the blank): you can see that by comparing the number of the counts and the values in the column "EP" (endpoint). If too noisy, and if after at least 5 min, the counts are higher than the blank, you can skip to the next step by turning the coulometric cell current off for a few seconds (or until the next count is made: it is every 30 seconds). Do not leave the cell current off too long, and do not do that except for the junks.

If the BLANK won't go down to ≤ 100 or stabilize

Check all gas connections in the system to see that there are any points where atmospheric CO₂ can get in. To check the quality of the inflow gas to see if this is the reason for the instability, disconnect the green tubing at the bottom of the system, right hand side of the titration cell. Connect the clear connector tubing (located in the "VINDTA spares" metal box in the cupboard under the system) from here directly to the tubing going in the coulometric cell (panel below stripper with two needle valves) and monitor the counts.

If the blank reading does not stabilize below 100 then it will be necessary to change the cell. Note that there will be another long stabilization time to consider. If the anode and cathode have been opened for too long, this might also be the source of high blank.

Unable to get BLANK value or clear and ready check fails because of instability of coulometer. Another reason for high blanks is a dirty frit in the stripper. Add phosphoric acid and leave. If the blank is still too high, you must change the scrubber.

Run a few JUNK samples before trying to get blank. Check system for potential leaks where atmospheric CO₂ could get in. Usually problem is due to exhaustion of input gas scrubber (see Section 5.3).

Zero blank

Due to no gas flow to cell or small blocks (precipitate) in the line to the cell (especially likely if the tube is new, otherwise the restricted narrowing has been snipped off the older cell lids.

Poor alkalinity reproducibility

This may be due to bubbles in the titrino tubing. Remove bubbles manually before turning the program on (or on another Titrino base), as once the program is on the Titrino is on remote mode so nothing can be done manually. To remove the bubbles, use the **DOS** and the **FILL (STOP)** buttons on the front panel of the Titrino, before turning the program on.

Back pressure in the system

Set the gas flow at 1.5 bar. If it is any higher then the tubes will pop off.

If the DIC gas flow does not register 150 ml/min there may be back pressure and the pipettes and stripper will not drain (undo the gas tube at the soda lime scrubber and re-run the method '3C DIC gas flow').

No gas flow at the start of the run

The 'set flow' yellow key may need to be selected – choose 149 ml/min to kick start the flow at the stripper and the cell. If there is no flow at all then check the cylinder (1.5 bar on top of regulator and over 50 bar in the tank. Also check the O-rings at the perchlorate and soda lime at the input to VINDTA 11 and VINDTA 24. If gas is leaking here then it is usually audible.

If gas flow into the coulometer stops or becomes slow

This may be due to the walls of the tubes sticking together (eg: valves 13 and 14).

Valve 13 compresses the stripper drain tube so nothing can pass through it. Remove it from the valve daily and roll between fingers to return to original shape.

There also can be obstructions in the outlet nozzle of the gas supply tube. Then it is necessary to remove the lid of the cathode cell and use a sharp point to remove blockages. After replacing the lid of the cathode cell and putting it back into the coulometer, it must be stirred/bubbled for >30 min to drive off all atmospheric CO₂ before turning on the cell current and continuing. If the DIC nozzle touches the side of the cathode cell this can cause a blockage, so ensure it does not.

Bubbles in tubing

To avoid bubbles, refill all reservoirs the day before using the system. To remove bubbles in the Titrino unit see above. For the tubing to the stripper, use the pull down controls:

3C DIC add acid>OTHER>OPEN bubbles are flushed out of the tubing and go into the stripper.

3C DIC drain stripper - the stripper is drained and during this process, the flow of nitrogen stops as this happens.

Bubbles in NaCl wash line

Remove tube from valve at entrance to VINDTA and fill via squeeze bottle of NaCl. Re-attach valve end then put free end straight under level of NaCl in carboy. Keep an eye on the levels of NaCl solution- when running many samples it is easy to let it get too low and end up with bubbles in the system.

Phosphoric acid delivery

If phosphoric acid is not delivered to the stripper – check level of acid in delivery bottle, check all connections and tighten as necessary. Check that the phosphoric acid pump is working. This is part number: 120SP2450-5TP from Biochem.Inc.

Investigating blocks

eg: stripper not emptying. Remove tube at valve (pull each end to remove). The stripper must be emptied using the individual methods after an aborted run.

Peltier cooler struggling to keep temp <5C

During run, occasionally empty the condenser:

‘IC drain condenser’ method

If the peltier cooler temperature doesn’t go down, this is probably due to a non-circulation from the waterbath. Check all tubing and connections as they might be blocked. The water circulation around the system should be visible. The system can be flushed using a long tube connected to the tap every few weeks to remove blockages.

Unusual readings for DIC

If the 3rd step of the titration is zero then the titration has occurred too quickly. This is due to gas flow – which must be set as low as possible. If the gas flow is too high some sample is lost to the far end of the stripper and will not be mixed with the phosphoric acid. A slow

decrease in values below the normal range will be an indication of the problem but by then the samples will be lost. The 'logfile.bak' records each stage of the DIC titration and can be reviewed to see the problem. Normal ranged for DIC are 2000-2250 uM/kg in the North Atlantic (2300-2450 uM/kg for TA).

Titrimo recording 0 μ mol/kg for TA

- Do not expect TA results when running JUNK samples
- check all connections between Titrimo, VINDTA control unit and computer. Note that when the Titrimo is switched between units then the cables (eg: stirrer) have to be switched too
- check levels of NaCl and KCl in outer and inner electrode cells respectively
- ensure magnetic stirring base is switched on
- re-boot the computer- it appears sensor connections sometimes 'fall out' if the PC has been left on for a number of days
- If the acid batch is new then check the concentration (1M rather than 0.1M for example results in no TA result).
- Sometimes at the start of the day the 1st TA reading may be zero as the Titrimo burette will refill after just 1-3 titration additions. It is best to restart the run (even though you will not get a DIC result produced).

Remember to empty the waste regularly to prevent it backing up into the titration cell.

SOFTWARE failure to abort process after pressing ABORT.

Sometimes it is necessary to exit the VINDTA program and even turn the computer off when the program is not responding. When the system is running, there is a red light showing "busy", and also a counter at the bottom of the window (left side) which gives how long the system has been on this task for.

Nothing can be done while the red light is on and the time is still running (the counter disappears when system is ready for the next task).

Do not abort a run unless absolutely necessary otherwise this will crash the program.

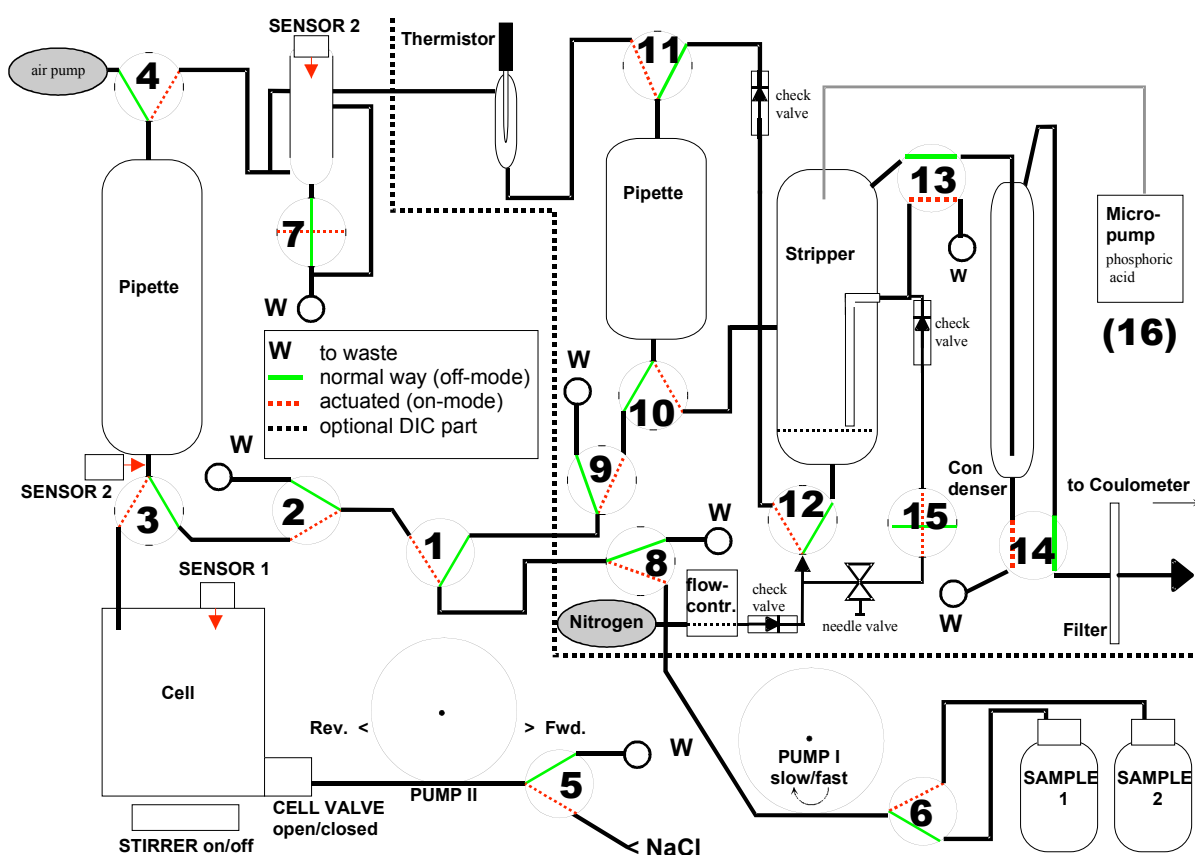
To shut down the program, use the **STOP PROGRAM** red buttons on each of the windows. It will close the program safely. When the window doesn't disappear by itself, close it using

the cross on the top-right corner if highlighted (it should be highlighted after you've pressed the STOP PROGRAM button).

Other software errors have been seen – for example the incorrect temperature readings show on the acquisition screen. Again it is best to restart the program (And the PC) if this occurs.

Moving and replacing the tubing:

1. The following drawing is in case you have to take some tubing out... Make sure you put the tubing back at the same place, as it is very important for the instrument to run properly. On the picture below, the green lines correspond to the back entry of each valve, and the red-spotted line to the front entry.



Coulometer not settling

- Is the Peltier cooled to less than 3°C? If not check for moisture in delivery tubes. If moisture is present then remove tubes, rinse with Milli-Q water and leave to dry overnight.
- Check gas delivery tubes for blockages
- Check cell is clean

- Is stirrer bar in cathode cell?
- Is gas flow or cathode obstructing light path?
- Is the gas bottle nearly empty? This does appear to cause problems with coulometer stability.
If so, source new bottle.
- The coulometer does have 'off' days where nothing seems to make it settle- if it doesn't work after an hour or two of trying it's highly unlikely it will settle that day.
- Are the DIC chemicals running low in the stock bottles – 'old' chemicals result in high blanks and these will need to be changed even if a few 100ml remain.

The logfile.bak is a text file appended for each sample. It is useful to look back at the behaviour of the coulometer. If there are more than 8 or 9 titration steps, or if the 3rd titration step is always zero, then there are clearly problems with the DIC titration. See appendix for troubleshooting tests on the UIC coulometer, to determine if the bulb or the photo-assembly and filter needs replacing.

Parameters that may affect Coulometer results

1. Position of the cell.
 - a. Light path is not blocked or affected by
 - i. Electrode
 - ii. Inlet or Outlet Tube
 - iii. Bubbles of gas
 - iv. The glassware too dirty.
2. The stirring bar is fouling the electrode.
3. The stirring bar is of the wrong size (use the large, wide stir bar)
4. The frit is dirty.
5. The instrument and/or cell is not up to temperature.
 - a. Run the cell for the correct "warm up" time as indicated in the manual.
(30 minutes)
6. The gas bubbles are too small.

Not reading correct %T

1. The solutions need changing.
2. The gas flow is too high.
3. No stirring bar in the cell.
4. Clean the frit with methanol and water.

Coulometer troubleshooting

1. A low %T can be caused by the following:
 - a. The lamps brightness has deteriorated with age and the lamp needs to be replaced.
 - b. The path to the detector is blocked.
 - c. The lamp voltage is incorrect.
- a. The detector and/or the filter have become clouded or the detector is defective.
- b. There is a loose connection on the CM110-020 Carbon front end Board.
- c. There is an electronic problem with the circuits on the CM110-020 Circuit Board.
2. The most common problem is 1 assuming you have checked to make sure there is no obstruction in the path of the cell (item 2). The lamp in your instrument, if it is the original, may have lost the ability to produce sufficient light after years of use. It is easily replaced. The housing holding the lamp unscrews and the lamp unplugs from the socket. This lamp is part number CM140-005.
3. If you replace the lamp and you still exhibit problems, the next thing to try would be the lamp voltage check item number 3. The lamp voltage check is in page 27 of the users manual. The lamp voltage is measured by using a digital voltage meter on test points TP7 and TP8 of the CM110-020 PCB. The lamp voltage is typically 2.00 VDC to 2.300 VDC. It cannot be greater than 2.50 VDC. The bulb will burn out!
4. To check and or adjust the lamp voltage, make sure there is no cell in the cell compartment. Turn the power off to the instrument and remove the left side panel. Locate the CM110-020 Carbon front end board. See figure 9.1 item K. At this time it would be wise to also make sure all the connectors to the CM110-020 are plugged in. The lamp power supply as well as the detector plug in here. Reset the connectors by pushing on them.
5. Attach a volt meter to TP7 (red) and TP8 (black) of the CM110-020 board. Turn the instrument on. Adjust the %T knob full clockwise. Measure the lamp voltage. If the lamp voltage is low adjust the potentiometer marked RV4 to increase the voltage. **Do not adjust the voltage above 2.5 VDC.**
6. If the %T is still low the next common source of this problem is the filter in the detector cell assembly has become clouded or the photo diode detector is defective. This sometimes happens when the unit has been in service for some time. The filter, Item CM140-001 can be replaced by itself. The photo diode is CM140-002. Replacing however the complete photo diode sub- assembly (CM101-178) is better because it eliminates the need for field assembly and soldering.
7. If these items do not seem to solve your problem, chances are there is an electronics problem on the CM110-020 board. In that case, a solution is to replace the CM110-020 carbon front end board. However, since the circuits are analog and a calibration is necessary, the CM110-020 cannot be replaced by itself without an electronic calibration. **For this reason it would be best to return the unit to UIC for this service.** The only other alternatives would be the purchase a Calibrated set of boards from UIC (CM101-139.) or a complete calibration kit of the filter, lamp, detector sub

assembly and a calibrated set of boards. The calibration kit is part number CM101-177.

How to install a new Detector cell Assembly CM101-134 into a CM5012 Coulometer.

- a. Unplug the Coulometer from the power source.
- b. Remove the Left side cover.
- c. Disconnect the assembly from the CM110-020 Carbon Front End P.C.B by :
 - i. Unplugging the P3 Plug.
 - ii. Unplugging the ground lug.
 - iii. Cutting the tie wrap holding the cable assembly.
- d. Locate the four 6-32 stainless steel socket head cap screws in the cell housing. Use a 7/64 inch socket wrench and unscrew the four socket head screws which hold the detector assembly in the cell housing. Hold the housing with your free hand while removing to avoid damage to the assembly.
- e. Remove the assembly from the instrument.
- f. To install the new assembly, reverse the procedure.

Procedure for checking the Electronics of a Carbon Coulometer

The following is a procedure to evaluate the electronics of a Carbon Coulometer. It requires the unit to be plugged in and turned on with no cell in the instrument. The Coulometer should be on for at least 10 minutes prior to testing to allow the electronics to stabilize.

Perform the Maximum and Minimum % T test:

Without a cell in the Coulometer, turn the % T knob fully clockwise and record the %T obtained. The % T should be greater than 100 %. The factory setting is 110 %. Please record the reading.

Maximum % T _

Rotate the %T knob fully counter clockwise and record the minimum %T obtained. The minimum %T is typically 12 % for a model 5012 Coulometer. Please record the reading.

Minimum %T _

Perform the Electronic Calibration Check on the coulometer:

This procedure is in the Coulometer Operation manual. It is repeated here for convenience.

Set the coulometer as follows:

Mode Selector switch to Mode 15 (or CALm). Set the Run/Latch switch to latch. Set the Count/time switch to count. Set the Time/set switch to 10.0 (In mode 15 this represents 10 seconds).

If the instrument is a model 5012, set the cell current switch to calibrate. If the instrument is a model 5011, install a shorting strap in the cell terminal and turn on the cell current.

Press the reset switch and let the electronics stabilize for at least 10 minutes.

Rotate the %T knob fully clockwise until 200 mA is displayed on the current display.

Every ten seconds the audible alarm will sound and the display should freeze at 100,000 \pm 500 counts. Record the results of 10 readings

1 Minute Calibration checks on Modes 1 -6:

If the instrument is a model 5012, set the cell current switch to calibrate. If the instrument is a model 5011, then install a shorting strap in the cell terminal and turn on the cell current.

Adjust the %T knob so cell current is at the maximum 200mA.

Set the coulometer as follows:

Set the Run Latch switch to latch. Set the switch to count. Set the Time/set switch to 1.0

Set the mode to 1 for your first reading and press the reset switch. Record your reading and then select your next mode, again pressing the reset switch. The modes and expected readings for each are as follows:

Based on a max current of 50mA, the calibration figures are as follows:

Mode 15 (counts) - 25,000 \pm 125 (for 10 second readings)

Mode 1 (ugC, 1 decimal place) - 373.5 (1 minute)

Mode 2 (ugC, 2 decimal places) - 373.44

Mode 3 (mgC/L) - 1867.3

Mode 4 (ugCO₂) - 1368.4

Mode 5 (ugCO₃) - 1865.8

Mode 6 (ugO) - 497.5

Evaluate the performance of the Current Coulometer Settings:

If the instrument is a model 5012, set the cell current switch to calibrate. If the instrument is a model 5011, then install a shorting strap in the cell terminal and turn on the cell current.

Open (model 5011) or remove (model 5012) the left side panel of the Coulometer (when facing the front of the coulometer).

Locate the CM110-019mainCoulometerboard. This is the top board of the two circuit boards located in the Coulometer on the left side.

Locate the toggle switch mounted on the main (top) circuit board. The normal position for this switch is in the center marked RUN. Change this switch to the position marked LO (to the left I back of the coulometer). This is the low current setting. See attached pictorial for location of this switch.

Observe the cell current display on the front of the Coulometer. It should read 2 mA. Please record the reading.

Toggle switch on LO (low current setting) (2 mA)

Change the switch to the setting marked HI (to the right front of the coulometer).

This is the high current setting. The current display on the front of the Coulometer should read 200 mA. Please record the reading.

Toggle switch on HI (high current setting)_____'(200 mA)

Make sure to put the switch back to the middle RUN position.

Evaluate the Current reduction system:

The following test is performed without a cell in the Coulometer.

If the instrument is a model 5012, set the cell current switch to calibrate. If the instrument is a model 50II, then install a shorting strap in the cell terminal and turn on the cell current.

With the %T knob at maximum clockwise rotation, the cell current display should be reading 200 mA (50mA with NOC modifications). Slowly rotate the %T knob counter clockwise until the cell current drops (199 mA). This should correspond to 62% ± 1 % T. Please record the response below.

Initial current reduction %T (62% ± 1 % T)

Continue rotating the knob slowly counter clockwise and record the cell current at the following points:

Cell current @ 50% T. ____ - ____ ^{130 ± 1.5)}
Cell current @ 40% T ____ ~ ____ ^{69 ± 5) TYPICALLY}
Cell current @ 35% T ____ 39 ± 5)

From the 35% T point, continue to slowly rotate the knob counter clockwise and observe the point at which the cell current goes to zero. This is called the cell current cutoff. It should be 29% T \pm 1% T and a cell current of 2 mA. The unit should be able to maintain a current of 2 mA with the %T just above the cutoff point. Please record the readings below.

Cell current cutoff (endpoint) __. %T (29% \pm 1% T)

Adjusting the cell current on the CM5014 Coulometer

This procedure provides details as to how to turn down the maximum cell current. Note that for DIC analysis the instrument is set at 50mA. This procedure will only need to be done if acquiring a new coulometer. The low current output will also need to be taken into consideration when performing UIC troubleshooting check on the coulometers.

The maximum cell current can be limited to a value less than 200 ma by adjustment of the “high course current” and the “high fine current” potentiometers located on the CM110-054 interface PCB. Values such as 50.0 ma can be set to be the maximum value instead of the factory standard of 200.00 ma.

Using the Cell current display, a value close to 50.0 ma can be set. Since the Coulometer integrates the actual current, the value not being exactly 50.00 ma will not alter the analytical performance of the instrument.

Procedure:

1. With the instrument off remove the left side panel by removing the 6 Phillips screws holding the panel in place.
2. Disconnect the ground wire and set the panel aside.
3. Locate the CM110-054 PCB in the lower section of the Coulometer.
 4. Locate the High Course potentiometer. It is the center potentiometer of 3 potentiometers just to the right of a toggle switch on the board. This potentiometer is labeled by the silkscreen of the board as RP5 and below it is HC in silkscreen. This stands for High Course current adjustment.
5. Locate the High fine potentiometer it is to the left of the RP5 High course potentiometer. It is labeled in silkscreen as RP6. Below the potentiometer is the label HF. This stands for High fine current adjustment. See photo 2
6. Warning! Do not adjust any potentiometers other than these. Adjustment of the wrong potentiometers will adversely alter the analytical performance of the instrument. If adjusted improperly, the instrument will require electronic bench calibration. This requires the Coulometer be returned to UIC or a calibrated set of boards be purchased.
7. Turn the instrument on. Be careful. Ac voltage is present as well as DC voltage. Use care when running the instrument with the covers off.
8. Run a cell setup without any cell in the Coulometer. Select the “RUN CELL SETUP” and press the ENTER key. Press F2 to accept the max value.
9. From the main menu select “RUN ANALYSIS” and press the ENTER key.
10. When the %T and CELL I display is present, turn on the Cell switch on the front of the Coulometer to “TEST”.
11. The % T will be 100.0 and the CELL I will be 200.0

12. Using a potentiometer adjustment tool or a jeweler's screwdriver turn the HC (RP5) potentiometer clockwise to lower the current from the 200.00 ma value to a value with in +/- 1 ma of 50.0. One turn clockwise lowers the current about 10 ma
13. Move the adjustment tool to the high fine adjustment potentiometer. It is labeled on the silkscreen as RP6. Below the potentiometer is the label HF. This stands for High fine current adjustment. Using the same method turn the HF (high fine Current adjustment) potentiometer counter clockwise to lower the cell current to a value of 50.0 ma.
14. When the display reads 50.0 for the CELL I the procedure is complete.
15. Turn the cell switch on the front of the coulometer to the off position.
16. The ESC key can be pressed 3 times to terminate the "RUN"
17. The instrument should be turned off.
18. The left side panel ground wire should be reconnected.
19. The left side panel should be re-installed.

6.6. VINDTA parts list

List updates available from Marianda web pages:

<http://www.marianda.com/downloads>.

VINDTA replacement and spare parts price list effective from June 2007, company name is listed and all prices are in Euros.

Made in house (ask for quotes):

Wooden rack 1
 Acrylic plate, main 1
 Acrylic plate, left 1
 Acrylic plate, right 1
 Acrylic plate, front 1
 Acrylic plate, pumps 1
 Acrylic plate, side connections 1

Mechanical parts

titration cell 1 OEM Marianda 1080.-
 flowcontroller 1 Sensirion (Vindta #010 - #012) Sensirion PC1NLOU1V_1N
 1 Bronkhorst (VINDTA #017 ---) Bronkhorst D-5111-FAB-BB-AV-22-0-S-A
 1 Aalborg (VINDTA #014 - #016) Aalborg GFC 173
 flowmeter 1 Aalborg (Vindta #003, #006 - #008) Aalborg GFM 17
 air pump FM 1101F 1 Fürgut Fürgut 116015
 peristaltic pump 2 OEM Marianda 1180.-
 servo (cell valve) 1 OEM Marianda 59.-
 auxillary electrode (Ti) 1 Marianda Marianda 20.-
 glass electrode 1 Thermo Orion Thermo Orion ROSS 8101 SC
 reference electrode 1 Metrohm Metrohm 6.0729.100
 valves 1-4, 8-11, 13-14 10 Biochem. Inc. Biochem. Inc. 075P3MP24-02B
 valves 5,6 2 Biochem. Inc. Biochem. Inc. 100P3MP24-05B
 valve 7 1 Biochem. Inc. Biochem. Inc. 100P2NO24-05B
 valve 12 1 Biochem. Inc. Biochem. Inc. 075T3MP24-32

valve 15 1 Biochem. Inc. Biochem. Inc. 075TNC24-62
acid pump 1 Biochem. Inc. Biochem. Inc. 120SPI24-50
mounting flange (big) 4 Biochem. Inc. Biochem. Inc. MF100
mounting flange (small) 14 Biochem. Inc. Biochem. Inc. MF075

Electronics

electronic box 1 Marianda Marianda ask for quote
Labjack USB controller 2 Labjack Labjack U12
solid state relays 24 Grayhill Farnell 70M ODC5
relay board 2 Labjack Labjack RB 16
circuit board V3/P0 (valve-relay connector) 1 OEM Marianda 140.-
circuit board V3/P1 (peristaltic pump control) 1 OEM Marianda 200.-
circuit board V3/P2 (servo control) 1 OEM Marianda 140.-
circuit board V3/P4 (level sensors) 1 OEM Marianda 240.-
circuit board V3/P7 (PT 100) 1 OEM Marianda 140.-
Peltier control unit 1 OEM Marianda 980.-
Peltier element, 35 W, 12 V 1 OEM Marianda 80.-
power supply, 24 V 1 OEM Marianda 100.-
power supply, 12 V 1 OEM Marianda 100.-
level sensor pipette (optical) 1 OEM Marianda 190.-
level sensor pipette overflow 1 Marianda Marianda 20.-
transformer for flowcontroller 1 Marianda Marianda 180.-
temperature sensor sample bottle (LM 34; grey) 2 Marianda Marianda 100.-
temperature sensor sample bottle (PT 100; white) OEM Marianda 130.-
temperature sensor small pipette (LM 34, screw M8) 1 Marianda Marianda 100.-
temperature sensor small pipette (PT 100, glass) OEM Marianda 120.-
temperature sensor cell (LM 34, transp.) 1 OEM Marianda 80.-
temperature sensor cell (PT 100, white) OEM Marianda 100.-
level sensor cell 1 OEM Marianda 79.-
various cables Marianda Marianda ask for quote

glassware

pipette big (AT) 1 OEM (glassblower) Marianda 190.-
pipette small (DIC) 1 OEM (glassblower) Marianda 150.-
stripper (DIC) 1 OEM (glassblower) Marianda 280.-
overflow vessel (AT and DIC) 1 OEM (glassblower) Marianda 90.-
acid trap (AT) 1 OEM (glassblower) Marianda 49.-
condenser (for metal block) 1 OEM (glassblower) Marianda 100.-
condenser (with thermostate jacket) 1* OEM (glassblower) Marianda 190.-

spare parts starter kit (only available with new VINDTA)

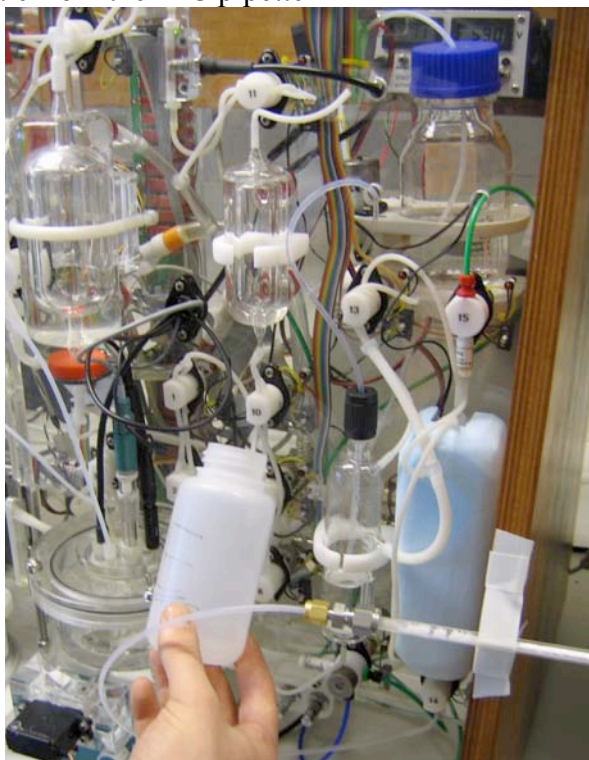
contains: glassware (big and small pipette, stripper, condenser, overflow, acid trap, condenser),
servo motor, cell full sensor, pipette empty sensor, Peltier element 990.-
OEM = 3rd party products custom made for Marianda
Fürgut: Fürgut GmbH Lärchenweg 12, D-88459 Tannheim, Germany (www.fuergut.com)
Biochem: look at www.bio-chemvalve.com for local supplier
Labjack: look at www.labjack.com for local supplier

Sensirion: look at www.sensirion.com for local supplier
Aalborg: look at www.aalborg.com for local supplier
Bronkhorst: look at www.bronkhorst.com for local supplier
Thermo Orion: look at www.thermo.com for local supplier
Metrohm: look at www.metrohm.com for local supplier
Farnell: look at www.farnellinone.com for local supplier
marine analytics and data

6.7. Additional VINDTA photo guides:

The following images are included to help users navigate around the VINDTA instrument

Filling a calibration bottle from the DIC pipette

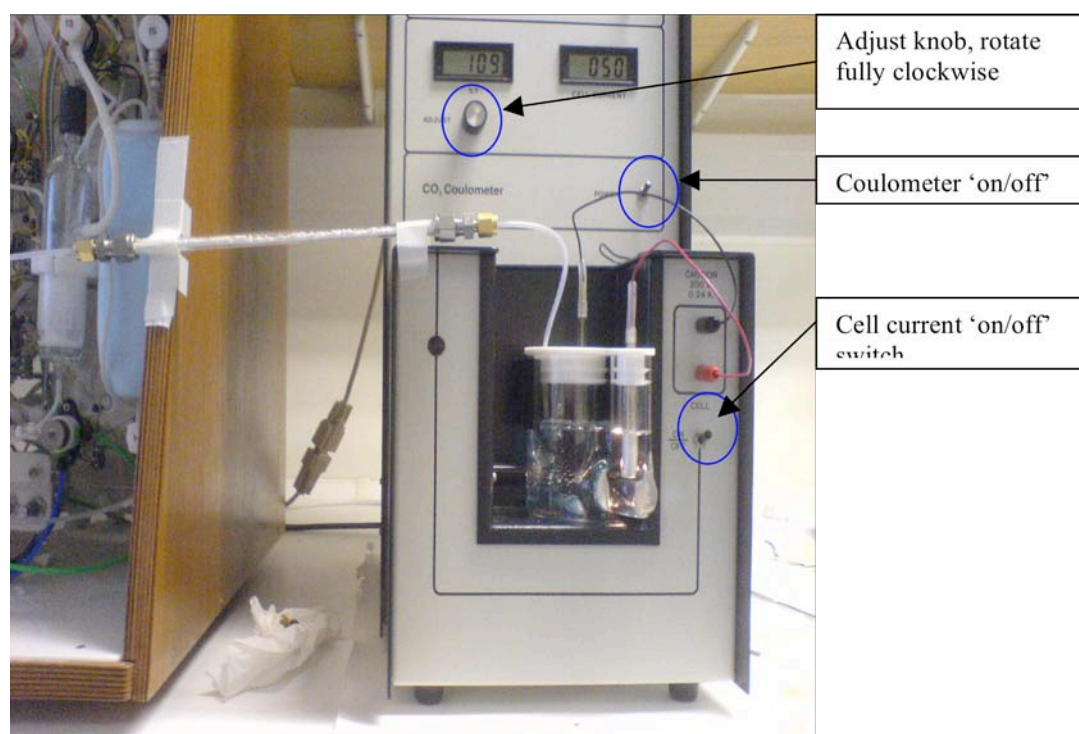


The Peltier condensing unit control box



The CRM input screen.

The details for batch 71 are already entered; only the individual bottle numbers need to be added.



The UIC Inc coulometer for DIC measurement

N₂ carrier gas bottle regulator valves.

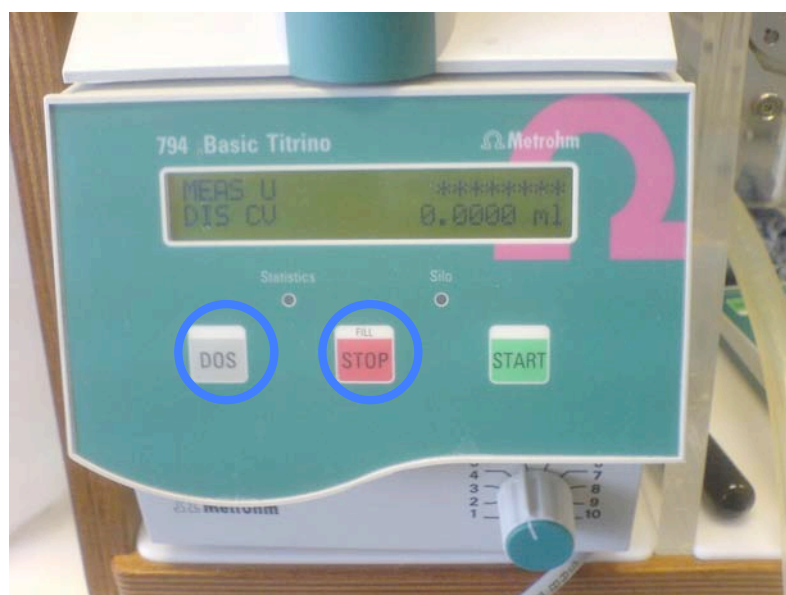
The central knob controls the rate of gas flow and should be set to ~1.5bar, the left hand and right hand knobs are both responsible for opening or closing the gas flow. Both should be opened fully when in use, and closed fully when not.



Ensure the gas is switched off using the gas spanner so your supply does not run out (switching off at the valves is not necessary).

Titrimo control panel

Highlighted are the 'DOS' and 'Fill' (the 'Stop') keys used to purge bubbles from the supply lines



6.8. Example of the CRM certificate of analysis and precision



University of California, San Diego
Scripps Institution of Oceanography
Marine Physical Laboratory
9500 Gilman Drive
La Jolla, CA 92093-0244

Certificate of Analysis

Reference material for oceanic CO₂ measurements

Batch #71 (Bottled on May 19, 2005)

This reference material consists of natural sea water sterilized by a combination of filtration, ultra-violet radiation and addition of mercuric chloride.

Analysis Results

The various procedures used for these analyses are detailed overleaf.

Salinity	33.923
Total dissolved inorganic carbon	$2032.84 \pm 0.40 \mu\text{mol}\cdot\text{kg}^{-1}$ (8; 8)
Total alkalinity	$2254.50 \pm 0.72 \mu\text{mol}\cdot\text{kg}^{-1}$ (21; 7)
Phosphate	$0.30 \mu\text{mol}\cdot\text{kg}^{-1}$
Silicate	$2.1 \mu\text{mol}\cdot\text{kg}^{-1}$
Nitrite	$0.00 \mu\text{mol}\cdot\text{kg}^{-1}$
Nitrate	$0.47 \mu\text{mol}\cdot\text{kg}^{-1}$

The cited uncertainties represent the standard deviation. Figures in parentheses are the number of analyses made (total number of analyses; number of separate bottles analysed). The nutrient levels may have changed on storage, their stability has not been examined. CO₂ analyses were performed over a period of time to confirm that the batch is stable.

The 95% confidence limits for the certified analyses are thus:

Total dissolved inorganic carbon	$2032.84 \pm 0.34 \mu\text{mol}\cdot\text{kg}^{-1}$
Total alkalinity	$2254.50 \pm 0.33 \mu\text{mol}\cdot\text{kg}^{-1}$

STORAGE: The bottles should be stored out of direct sunlight, and preferably at or below room temperature (25 °C). They should not be allowed to freeze!

Andrew G. Dickson
January 4, 2006

6.9. Risk assessment for the VINDTA 3C

Room No	Compressed gases	Flammable Substances	Toxic substances	Corrosive substances	Comments
494/12	Nitrogen size W cylinder x2				
494/12		Acetone 2.5L			
494/12			Mercuric chloride contained in each seawater sample and waste 0.0007%		
494/12			Mg(ClO ₄) ₂ 250g		
494/12				HCl 2.5L plus 12x 100ml ampoules of 1M HCL	
494/12			Soda lime 500g		
494/12				Phosphoric acid 2.5L	
494/12				Ethanolamine 5% in cathode solution (1gallon containers x 3)	
494/12				Nitric acid 2.5L	
494/12		Methanol 2.5L			
494/12				Decon cleaner 2.5L	

Assessed by Sue Hartman, 20/2/2009

Sign and date when read and understood:

Introduction: This risk assessment concerns the analysis of alkalinity and total carbon using the VINDTA system. This is purpose built equipment does a titration of seawater with dilute hydrochloric acid and adds phosphoric acid to another sample to drive off CO₂. Procedures are described in maker's manual and an NOC manual available in the laboratory.

	Hazard	Precautions taken	Further action
Activity 1. Lifting boxes	Sample boxes weight approx 20kg	Avoid lifting if possible. Lift with care.	Use safety boots.
Activity 2. Gas bottles	Lifting the gas bottles (weight approx 40kg) into place	A gas trolley must be used for transport and the canisters must be secured to the laboratory bench.	Use safety boots when moving gas bottles
Activity 3. Use of chemicals	Soda lime Magnesium perchlorate Hydrochloric acid Phosphoric acid DMSO Ethanolamine Tetraethylammoniumbromide Thymolphthaleine Acetone Mercuric chloride	Wear gloves when handling the samples (which contain trace amounts of mercuric chloride added at the point of sampling). Wear gloves to prepare the cell and when using all chemicals. Ensure the laboratory is well ventilated	Follow the chemical datasheets attached for action in the event of a spillage. Treat spills of samples that have been preserved as toxic.
Activity 4. Inspecting for leaks	Sprays and leaks from complex tubing circuits under gas pressure are possible.	Wear eye protection and gloves	Keep the gas lines clean and inspect the valves frequently to avoid any back pressure
Activity 5. Laboratory procedures	Sample or chemical spills	Have plenty of absorbent tissue handy to contain any spills. Tissue from sample spills should be disposed (via NOC Facilities) of as it has trace contamination of mercuric chloride.	Follow the chemical datasheets attached for action in the event of a chemical spillage
Activity 6. Use of the computer	Danger of spilt liquids. Overuse of VDU	Avoid using chemicals near the computer. Do not use gloves on the keyboard to avoid transfer of chemical and samples. Follow good VDU practice and leave the screen for frequent breaks.	

Detailed risk analysis for each activity

Activity 1. Lifting boxes
Participants: David Hydes, Sue Hartman and students in the lab.
Location: 494/12
Frequency of activity: daily
Substances used:
Activities performed: Lifting boxes of samples
Hazards: foot and back injury possible
Existing control measures: use a trolley, get assistance lifting
Assessment of risk: The risks associated with this process are small, assuming that good lifting procedures are followed.
Action required: Use foot protection.

Activity 2. Gas bottles
Participants David Hydes, Sue Hartman and students in the lab.
Location 494/12
Frequency of activity: monthly
Substances used: nitrogen cylinders weighing approx 40kg
Activities performed: Lifting and securing in place
Hazards: Heavy load
Existing control measures: Use a gas trolley. Strap the canister to the bench.
Assessment of risk: The risks associated with this process are small, assuming that good lifting practice is followed.
Action required: Use foot protection.

Activity 3. Use of chemicals
Participants: David Hydes, Sue Hartman and students in the lab.
Location: 494/12
Frequency of activity: daily
Substances used: Soda lime Magnesium perchlorate Hydrochloric acid Phosphoric acid DMSO Ethanolamine Tetraethylammoniumbromide Thymolphthaleine Acetone Mercuric chloride
Activities performed: soda lime and Magnesium perchlorate loaded into glass tubes as drying agent. Other chemicals are diluted in the laboratory, except for Mercuric chloride, which is added at the point of sampling and is a low level contaminant of the samples. Preparation and cleaning the coulometer cell involves use of organic chemicals. A DMSO and ethanolamine vapor is given off by the cell
Hazards: spillage of chemicals, glassware breakage, chemical ingestion, breakage of equipment
Existing control measures: Wear gloves, do not eat or drink, handle glassware carefully, ensure the laboratory is well ventilated
Assessment of risk: The risks associated with this process are small, assuming that common sense and good laboratory practice is applied
Action required: In the event of a spillage follow the instructions on the attached chemical hazard data sheets.

Activity 4. Inspecting for leaks
Participants: David Hydes, Sue Hartman and students in the lab.
Location: 494/12
Frequency of activity: weekly
Substances used: None
Activities performed: Inspection of valves and tubing.
Hazards: If the system blocks the tubes can come off and liquid leaks out of the VINDTA if the system has not been used for a while
Existing control measures: Wear gloves and safety glasses
Assessment of risk: The risks associated with this process are small, assuming that adequate protective wear is worn.
Action required: Use gloves and eye protection. In the event of leaking sample or chemicals collect the waste for toxic waste disposal.

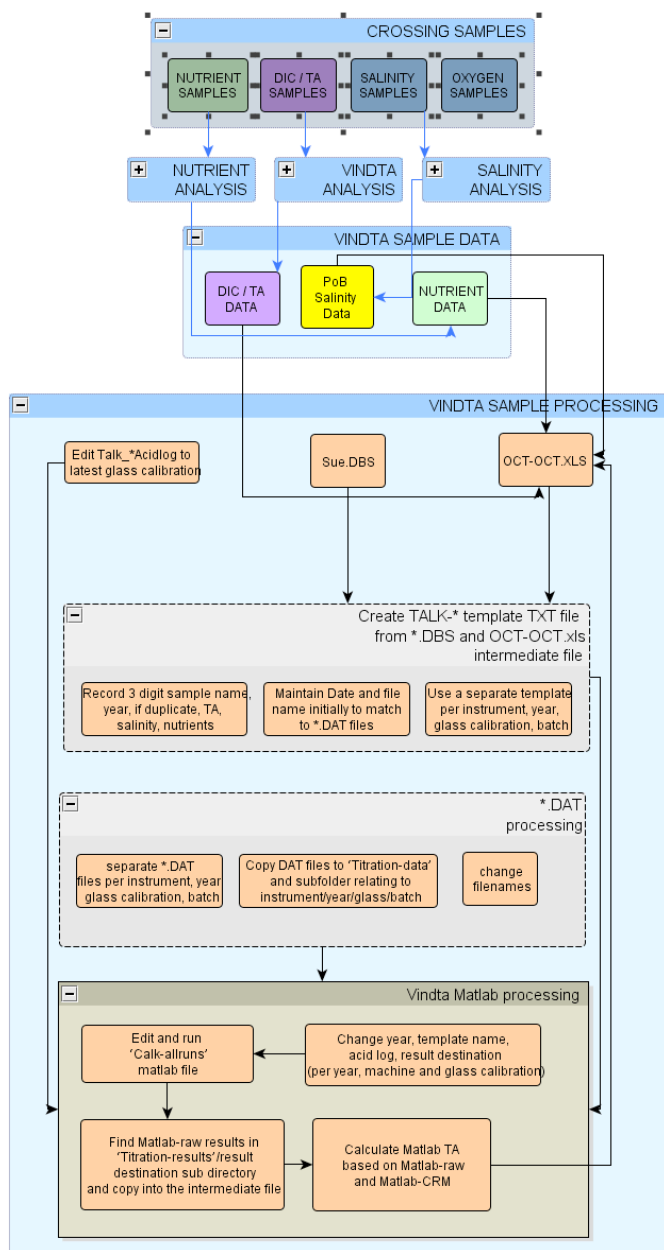
Activity 5. Lab work including sample spills and waste disposal
Participants: David Hydes, Sue Hartman and students in the lab.
Location: 494/12
Substances used: Handling samples and waste with low concentrations of mercuric chloride. Waste from the coulometer cell with DMSO and ethanolamine.
Activities performed: Disposal and waste and cleaning up spills of samples and chemicals
Hazards: spillage of chemicals, glassware breakage, chemical ingestion
Existing control measures: Wear gloves, do not eat or drink, handle glassware carefully. Wear a lab coat/boiler suit and safety glasses.
Assessment of risk: The risks associated with this process are small, assuming that good laboratory practice is followed.
Action required: In the event of a spillage follow the instructions on the attached chemical hazard data sheets. Dispose of any waste as a low level toxin via Facilities procedures in place.

6.10. Sample processing

A) MATLAB processing of TA

The flow chart below shows the files that are necessary before processing the TA data. An interactive version of the flowchart can be found on the Shared drive:

S:\OBE\ferriybox\Vindta flowchart\VINDTA v1.1.html



Matlab template

% A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	PO4	NO3	TCO2	TA
Analysis	Year	Month	Day	Hour	Min	Station	Casting	Bottle ID	Bottle AB	Depth	FlagT A	Batch acid	Temp _insitu °C	Salinity	SiO4 (umol/kg)	(umol/kg)	(umol/kg)	(umol/kg)	_raw_curve_fit_May08_Vindta (umol/kg)
1	2007	4	17	17	45	71	1	789	1	0	3	106	25	33.92		2.10	0.30	0	2333.83
2	2007	4	17	18	13	704	1	64	1	5	3	106	25	30.02	6.00	0.00	0	0	2319.26

Line 2: example for CRM

Line 3: example for a sample

Column B, C, D, E, F: date and time of analysis. Found on the .dbr file.

Column G: for CRM put the batch number; for the sample we agreed for the POB samples to put year and month of the crossing (in this case it would be April 2007 crossing) however, to prevent any problems with matlab we need to run each year separately, i.e. 2008, 2009... so make a different spreadsheet for each year

Column H: not relevant for the POB samples or underway samples (just put 1 for all samples)

Column I: for CRM put the bottles number (!!! Only 3 digits!!! the one on the left side of the sticker); for the sample we put the number of the sample for the specified crossing

Column J: in case of replicates, put 1, 2, 3... ; keep the same sample ID

Column K: depth

Column L: degree of confidence in the measurement

Column M: in the future this will change every time a new batch of acid will be made (if titrated) and the value entered in the VINDTA program.

For now this is the same for all samples even if the acid has been changed (the acid concentration hasn't been changed in the software.

You can check this in the .dbr file, the acid concentration used should be the same for all samples, it should be 0.099)

Column N: temperature of measurement (25)

Column O: real salinity of your sample

Column P, Q, R: nutrient concentration

Column S, U, V, W, X, Y, Z: not used in our case as this is to recalculate DIC

Column T: Alkalinity value given by the program (the curve fit one which is also the one appearing on the screen)

Acid log template

The pipette volume will need to change and the acid concentration will also vary. The acid factor was changed on VINDTA 24 on the 17th Aug 2009 (to 0.0878 mol/kg) although the acidlog file uses an acid concentration of 0.099 mol/kg (and density 1.0227 kg/l).

The pipette volumes for unit 11 are as follows: In May 2009 the volume changed from 97.592 ml to 97.577 ml. On the 3/6/09 it decreased to 95.023 ml due to a change in glass; then on 21/8/09 changed to 95.088 ml. On the 23/9/09 the volume should have been changed to 94.996 ml (although it wasn't changed in the VINDTA software immediately in error); on the 9/10/09 the volume decreased slightly to 94.992 ml and to 94.939 from 27/8/2010.

For unit 24 the TA pipette volumes changed as follows: 97.989 ml on 24/6/09 (as the unit was supplied with incorrect glass calibrations). Calibration checks on the 2/7/09 showed the volume to be 105.043 ml. When the glass was changed on 28/10/09 the new TA pipette volume was 97.409 ml.

Acid log file					
%Acidbatch	Year	Month	Date_start	Hour_start	Min_start
Pipetvolume(ml)	Acidconc (mol/kg)		AcidDens (kg/l)		AcidSalt (g/liter)
106	2008	7	28	13	0
97.592		0.099		1.0227	41

Calcalk_allruns matlab file, note parts in BOLD which need to be altered code from Dorothee Bakker, UEA

```
%read_alkfiles.m
%read alkalinity data from Vindta *.dat files
clear,clc
close all;

%Select carbonate constants for AlkConstants.m
Roy = 1; Prieto = 2;
CK = Prieto %Use constants by Prieto and Millero (2002)

cd ../../POB
load Talk_allrunsc.txt -ascii; %POB
load Talk_Acidlog.txt -ascii; %POB
cd ../matdoro/alkalinity/alkalinity_vindta
runs = Talk_allruns;
```

```

acid = TAlk_Acidlog;
clear TAlk*;

%list files in directory with dir command
D = dir(' ../../POB/Titration_data/SNOMS_08suhdatac/*.dat') %for subdirectory
%Or make file with all the file names
st = NaN * ones(length(D), 1);
Nis = NaN * ones(length(D), 1);
Rep = NaN * ones(length(D), 1);
testlines = NaN * ones(length(D), 1);
restot = NaN * ones(length(D), 39);
for pq = 1:length(D)
%read data file name and open file
fname = D(pq).name
eval('fname');
% open data file in subdirectory
cd ../../POB/Titration_data %subdirectory
fid_datafile = fopen(fname,'r');
[junk] = fgetl(fid_datafile);
[junk] = fgetl(fid_datafile);
% read the data
data = fscanf(fid_datafile,'%f');
cd ../../matdoro/alkalinity/alkalinity_vindta
ndata = length(data)/3; %3 for 3 columns
%reorganise data vector into an array
data2 = reshape(data, 3, ndata);
data2 = data2';
fclose(fid_datafile);
testlines(pq) = length(data2);
% VOL = data2(:, 1); %Volume of acid added (ml)
% EMF = data2(:, 2); %EMF reading electrode (mV)
% Temp = data2(:, 3); %Temperature (degrees Celsius)
%
%Read station/type, Niskin/bottle, Repeat/Run from file name
sname = eval(fname(1:2));

if sname == 10 %sample Ischia ** this is the year that the sample was taken, ie: 2010 in
this case **
    st(pq) = eval(fname(1:4));
    Nis(pq) = eval(fname(8:10)); %N.B. NEW position characters in Visual Basic!!
    Rep(pq) = eval(fname(15)); %N.B. Not true replicates ???

elseif sname >= 67 %CRM batch 67 Ischia, dummies batch 76
    st(pq) = sname;
    Nis(pq) = eval(fname(6:8)); %NEW position in Visual Basic output
    Rep(pq) = eval(fname(13)); %NEW position in Visual Basic
end %if sname
clear sname;

```

```

%----end of reading data file and file name-----

%---find titration data-----
VOL = data2(:, 1); %Volume of acid added (ml)
    EMF = data2(:, 2); %EMF reading electrode (mV)
%      Temp = data2(:, 3); %Temperature (degrees Celsius)
%CD6
    Temp=zeros(size(data2(:, 3)))+25;

NPoints = length(VOL);
TempC = Temp(1); %Temperature (degrees C)

%clear fname fid_datafile data data2 ndata junk;
acidbatch = NaN;
%find nutrients, salinity
for k = 1:length(runs)
    ind1 = find(runs(k, 7) == st(pq) & runs(k, 9) == Nis(pq) & runs(k, 10) == Rep(pq));
    if ind1
        acidbatch = runs(k, 13);
        Sal = runs(k, 15);
        T(4) = runs(k, 17) * 10^-6; %PO4
        T(5) = runs(k, 16) * 10^-6; %SiO4, convert umol/l to mol/l

        restot(pq,1:22) = [runs(k, 1:21) Temp(1)];
        %find pipetvolume, acidconcentration, acid density
        [m, n] = size(acid); %NEW 02/07/07
        for s = 1:m %NEW 02/07/07 (for s = 1:length(acid), problem for short acid
columns)
            ind2 = find(acid(s, 1) == acidbatch);
            if ind2
                VPipet = acid(s, 7); %Pipette volume (ml)
                AcidRho = acid(s, 9); %Density acid (kg/l)
                AcidConc = acid(s, 8); %Concentration acid (mol/kg_solvent)
                restot(pq, 23:25) = [VPipet AcidRho AcidConc];
            end %ind2
            clear ind2;
        end %s
        clear m, n; %NEW 02/07/07
        if ~isnan(T(4))
            vindta_calc %mfile - call alkalinity calculation routine
            %Gran = [GranIterate TA*10^6 TC*10^6 RMS*10^6 Enot pK1 VV11 VV22]
            %MLSQ = [Iterate TA*10^6 TC*10^6 RMS*10^6 Enot pK1 Trial NaN]
            len1 = size(Gran,1); %number of rows
            len2 = size(MLSQ, 1); %number of rows
            restot(pq, 26:40) = [Gran(len1,1:8) MLSQ(len2,1:7)];
            clear len1 len2;
            clear Gran MLSQ;
            clear acidbatch Sal T VPipet AcidRho AcidConc Sal VOL EMF VOL;
        end
    end
end

```

```

end

end %ind1
clear ind1;
end %for k
clear k;
end %for pq;
clear pq;
restot(:, 7) = st;
restot(:, 9) = Nis;
restot(:, 10) = Rep;s
cd ../../POB/Titration_results
save Talk_all_results.txt restot -ascii;
cd ../../matdoro/alkalinity/alkalinity_vindta

%clear restot;
%clear st Nis Rep;
%clear acid D runs;
clear TCInitialGuess;
clear CK;

```

B) DIC- Coulometer Calculations – Counts to $\mu\text{mol CO}_2/\text{kg}$

The formulas below show how we convert coulombs (the unit that the coulometer really measures) to counts of Carbon and CO_2 (the unit that the software uses).

1 Faraday = 96,485.34 coulombs
 12.011 g Carbon = 96,485.34 coulombs
 44.01 g CO_2 = 96,485.34 coulombs

12.011 mg Carbon = 96.48534 coulombs
 44.01 mg CO_2 = 96.48534 coulombs

1 mg Carbon = 8.033 coulombs
 1 mg CO_2 = 2.192 coulombs

1 coulomb = 1 Amp-sec

1 mg Carbon = 8.033 Amp-sec
 1 mg CO_2 = 2.192 Amp-sec

1 μg Carbon = 8.033 mA-sec
 1 μg CO_2 = 2.192 mA-sec

1 count = 0.02 mA-sec

1 μg Carbon = 401.65 counts

1 μg CO_2 = 109.62 counts

Since we now know how many counts are equivalent to a microgram of Carbon or CO_2 , we can convert counts to micromoles of CO_2 .

1 mol CO_2 = 44.01 g

1 μmol CO_2 = 44.01 μg

44.01 μg CO_2 = 4824.38 counts

1 μmol CO_2 = 4824.38 counts

The software reads the counts from the coulometer to first determine the endpoint of the analysis. The final count reading is used in the calculations. You will need to check with Ludger for his exact calculations, but the following is how we calculate the final result.

A simplified equation:

Final result = ((Final Reading) – (Corrected Blank Value)) / Sample Size

Where:

Final Reading = The last coulometer reading

Corrected Blank Value = The blank value as a function of the number of readings. The blank is established over a set number of readings, but the analysis may take longer than the number of readings used to determine the blank value. In these cases a Corrected Blank is calculated based on the following formula: Corrected Blank Value = (Blank Value / Number of Blank Readings) x Number of Analysis Readings

Sample Size = The size of the sample expressed as a weight or volume

An equation specific to μmol CO_2/kg :

$$\mu\text{mol CO}_2/\text{kg} = (((\text{Final Reading}) - ((\text{BV} / \text{NRB}) * \text{NRA})) / 4824.38 \text{ cts}/\mu\text{mol CO}_2) / \text{kgSample}$$

Where:

Final Reading = Final coulometer reading in counts

BV = The total blank value in counts

NRB = The number of readings used to determine the blank

NRA = The number of readings taken during the analysis

KgSample = The weight of the sample in kilograms

Sample Calculation:

Final Reading = 193,025 counts

BV = 50 counts

NRB = 10

NRA = 10

KgSample = 0.020 kg

$$\begin{aligned} \mu\text{mol CO}_2/\text{kg} &= (((193,025 \text{ cts}) - ((50 \text{ cts} / 10) * 10)) / 4824.38 \text{ cts}/\mu\text{mol CO}_2) / 0.020 \text{ kg} \\ &= ((193,025 \text{ cts} - 50 \text{ cts}) / 4824.38 \text{ cts}/\mu\text{mol CO}_2) / 0.020 \text{ kg} \\ &= (192,975 \text{ cts} / 4824.38 \text{ cts}/\mu\text{mol CO}_2) / 0.020 \text{ kg} \\ &= 40.0 \mu\text{mol CO}_2 / 0.020 \text{ kg} \\ &= 2000 \mu\text{mol CO}_2/\text{kg} \end{aligned}$$

The DIC readings from the VINDTA need to be converted to $\mu\text{mol/kg}$ once the salinity data are known using the following formulae.

A	B	C	Depth (m)	E	F	G	H
Sample ID				VINDTA results			
	lat N	long E	Depth (m)	DIC raw	TA raw	Temp	Salinity
UW1	51.49943	1.82679	5	2110.82	2387.02	16.38	35.02
UW2	51.84352	2.19394	5	2109.60	2393.81	16.08	35.20

I	J	K	L	M	N	O	P	Q
					CRM Corrected results		Finalised data	
VINDTA temp	term 1	term2	term 3	Density 25C	DIC crm corr	recal TA crm corr	DIC sal corr	TA sal corr
25	0.0007592	4.202E-06	4.831E-07	1.0263	2087.15	2330.10	2087.13	2330.10
25	0.0007592	4.202E-06	4.831E-07	1.0264	2086.90	2328.06	2086.60	2328.06

term 1 input = $8.24493 \times 10^{-4} - 4.0899 \times 10^{-6} \times I3 + 7.6438 \times 10^{-8} \times (I3^2) - 8.2467 \times 10^{-10} \times (I3^3) + 5.3875 \times 10^{-12} \times (I3^4)$
term 2 input = $-5.72466 \times 10^{-6} + 1.0227 \times 10^{-7} \times I3 - 1.6546 \times 10^{-9} \times (I3^2)$
term 3 input = 4.8314×10^{-7}
density at 25 = $1 + J3 \times H3 + K3 \times H3^{1.5} + L3 \times H3^2$
DIC salin corr = $N3 \times 1.0263 / M3$
TA sal corrected = O3

6.11. Contact details:

Susan Hartman Responsible for the NERC NOCS VINDTA instrument.

Contact for general enquiries eg: parts, chemicals, booking equipment, troubleshooting and gas bottles. Internal Extension: 26343, Room number: 494/14, E-mail: suh@noc.soton.ac.uk

Bob Clarke at RS Slaughter is the UK contact for the Coulometer contact:

bob@slaughter.co.uk

Ludger Mintrop Builder of the VINDTA instrument, all major operating enquiries should be directed to Ludger.

Telephone; +49 (0) 431 719497-39, Fax: +49 (0) 431 719497-69,

e-mail; info@marianda.com

Postal address: Tulpenweg 28, D-24145 Kiel, Germany

Useful manuals:

For more detailed information check the following alternative manuals:

C:\VINDTA\documents\VINDTA 3 manual V3.01 (Ludger Mintrop)

C:\VINDTA\documents\VINDTA_Manual_update.doc

